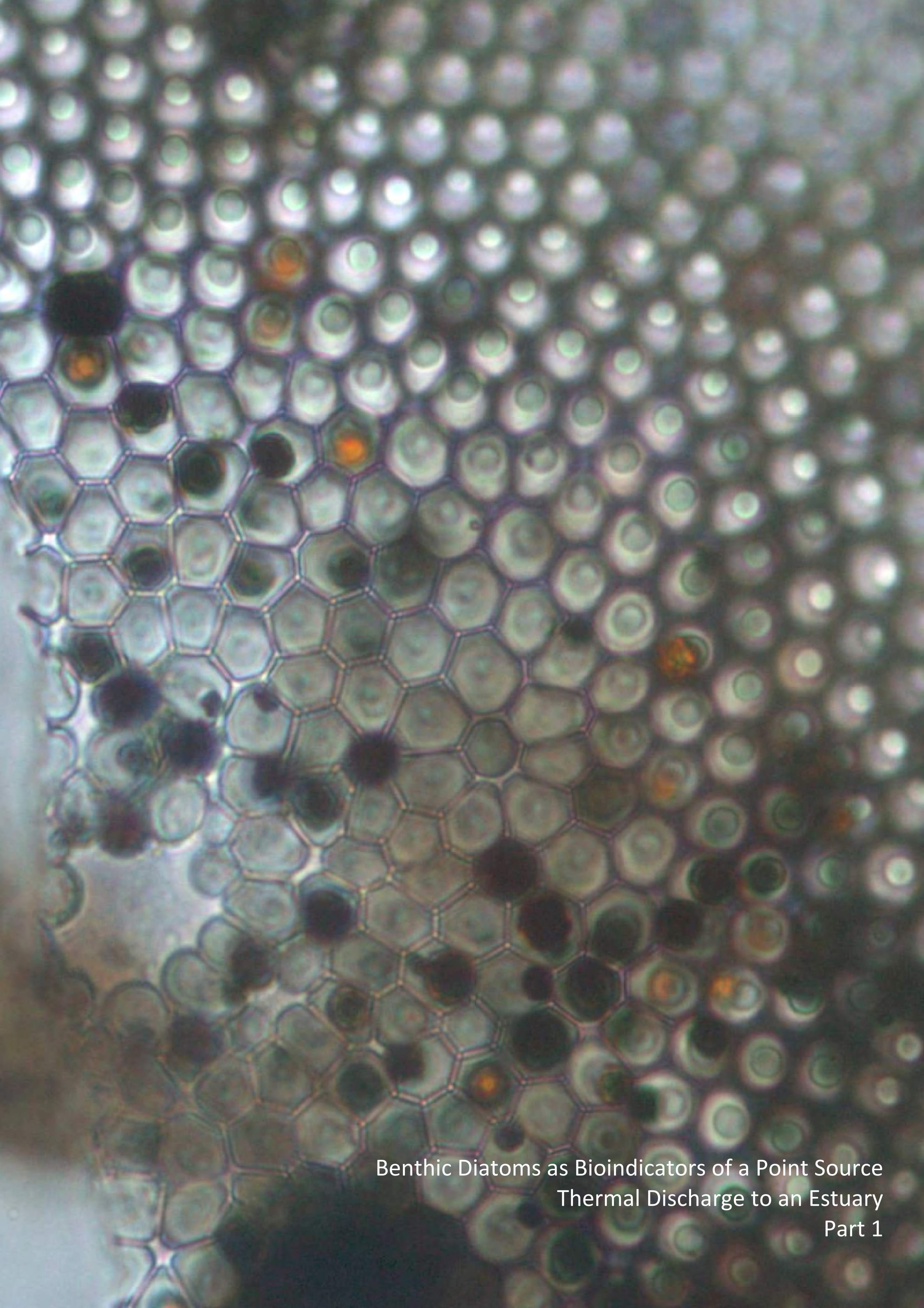

Benthic Diatoms as Bioindicators of a Point Source Thermal Discharge to an Estuary
Part 1

Statement of Co-Authorship

The following people and institutions contributed to the publication of the work undertaken as part of this thesis:

Paper 1 Thermal Plume Effects: A multi-disciplinary approach for assessing effects from thermal pollution on estuaries using benthic diatoms and satellite imagery.

Ingleton (90%), McMinn (10%)

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Details of the Authors roles:
Author 1 formulated the idea, completed the fieldwork, labwork and statistical analyses and production of the manuscript text and figures
Author 2 assisted with refining the sampling strategy, taxonomy and refinement of the manuscript for submission

We the undersigned agree with the above stated "proportion of work undertaken" for each of the above published (or submitted) peer-reviewed manuscripts contributing to this thesis:

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Benthic diatoms as bioindicators of a point source thermal discharge to an estuary

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Bachelor of Science (Hons)
Submitted in fulfilment of the requirements for the degree of Doctor of Philosophy
University of Tasmania
May 2012

Declaration of originality
This thesis contains no material which has been accepted for a degree or diploma by the University or any other institution, except by way of background information and duly acknowledged in the thesis, and to the best of the my knowledge and belief no material previously published or written by another person except where due acknowledgement is made in the text of the thesis, nor does the thesis contain any material that infringes copyright.

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The thesis presented here is written as a series of scientific research papers in preparation for journal publication. At the time of thesis final submission only Paper 1 had been accepted for publication. The paper “Thermal Plume Effects: A multi-disciplinary approach for assessing effects from thermal pollution in estuaries using benthic diatoms and satellite imagery” was published in March 2012. A diatom species catalogue and taxonomic database is presented in the appendices Part 2.

Australian Higher Education Graduation Statement (AHEGS) Abstract

Monitoring the effects of thermal point source discharges to coastal lakes is important as a measure of system health and to manage the effects of elevated temperature on the receiving environment. Currently, 3 coal-fired power stations on the New South Wales central coast utilise lakes as source and sinks for cooling water discharging at up to 12 °C above ambient. Surficial sediment samples and cores from an embayment receiving a thermal discharge from a power station and control embayments were analysed for benthic diatoms. While a range of species were associated with the plume gradient, *Navicula rhaphoneis* identified areas of thermal pollution at the lake bed >3-4 °C above ambient. Multi-variate statistical analyses indicated that the key variables governing diatom distribution were temperature, nutrients, selenium and salinity. Temperature data indicated that thermal pollution was greater in autumn-winter than summer-spring. Fossil diatoms analysed from cored sediments indicated shifts in assemblages associated with changes in power station capacity. A reference dataset obtained for central coast lakes was used to develop diatom-based models (WA/PLS/WAPLS) and conduct palaeoecological reconstructions for the dominant independent variables – temperature, salinity and phosphate. Longer-term water quality monitoring data was used to validate the models and indicated that salinity and temperature had been relatively lower for the period preceding power station commissioning. Although temperature changes over time were likely associated with shifts in assemblages, they were difficult to delineate from regional temperature change using this reference dataset.

As a means to improve the diatom-inferred transfer function, a secondary latitudinally-based (temperature proxy) reference dataset was developed using benthic diatoms acquired from lakes from Noosa (26 °S) to Eden (34 °S). Iterations of the multi-variate analyses were performed on six different forms of the reference dataset as a means of sensitivity testing varied on the basis of taxonomic resolution, number of species and number of sites/sampling design. The nested dataset (nTL1) provided improved model performance metrics (r^2, r^2p, RMSEP) and temperature reconstruction standard errors. Correlations between diatom-inferred temperature and long-term temperature data indicated that the

relationship for the nested dataset was closest to being significant at $r^2=0.33$ ($n=28$, $p<0.05$) compared to others tested.

To provide a greater temporal perspective of fossil assemblages and contributing metal contamination, cores were obtained from a point closer to the discharge as well as control location for ^{210}Pb, fossil diatom and heavy metal analyses. Elevated concentrations of metals sourced from the northern lake and identified in sediments lake-wide, provided an additional marker for validation of the lake-sediment chronology. Only sediments within the control bay core were adequately preserved for dating. Metal profiles indicated that metal enrichment at the control location (Cd, Cu, Zn) commenced around 1925. Pre-industrial sediments were then targeted for benthic diatom analyses to infer control bay pre-condition. Comparisons between plume effected and control location assemblages indicated that both the receiving water and control bays possessed similar assemblages during this time and likely to have experienced similar environmental conditions.

Thesis abstract

The work presented here describes a novel approach for determining past and present effects of a power station thermal plume discharge on an estuary. The technique utilised benthic diatoms, combining palaeoecological and contemporaneous multi-taxa approaches, to demonstrate that diatoms were not only responding to the plume in the modern day environment, but also indicated a changing temperature regime within the receiving water bay over time. The approach provided new information and demonstrated a range of techniques that may be employed for improved management of thermal discharges to enclosed coastal water bodies.

To determine the spatial distribution of benthic diatoms in relation to a power station cooling field, the discharge at Vales Point, Lake Macquarie, was selected as the study site and first sampled in 2003. The initial fieldwork sampled sediments along a thermal gradient with increased distance from the discharge point. This spatial pattern was then replicated within two other southern lake control embayments. Multi-variate analyses determined that temperature and a number of other variables associated with the plume explained gradients in the diatom flora of the receiving bay. Satellite imagery and high resolution logger data then provided detailed plume and lake temperature information and indicated that thermal loading of lake water and thus the potential for ecological effects were expected to be greater in autumn/winter compared to summer.

To determine changes in receiving bay water quality over time and to establish pre-power station baseline conditions, a sediment core was obtained from Wyee Bay, sub sectioned, ^{210}Pb dated and analysed for fossil benthic diatoms. Diatom-inference models were then developed based upon a localised reference dataset obtained from sample sites across Lake Macquarie and NSW central coast estuaries. The assemblage profile displayed periods (several years to decades) of relative homogeneity and heterogeneity (years to a decade), co-incident with the major phases of power station operation. A change in assemblages was also observed around 1925-30 and prior to power station commissioning, indicating a change to receiving bay ecology at an earlier time. Although the salinity and temperature data were both

adequate for modelling, reconstruction errors meant that only longer-term trends were discernable for temperature. When compared to real-time data (monitoring) variability in salinity within the core was relatively well represented by the model and appeared to respond to climatic factors such as SOI and rainfall. Longer-term salinity trends, however, were not as reliable as those for temperature.

In an effort to improve the temperature-inference model for the Wyee Bay core an alternative reference dataset was developed by sampling across a natural temperature gradient. Triplicate samples from 13 estuaries from Noosa (southern Queensland) to Eden (southern NSW) (26 °S – 37 °S) were analysed for benthic diatoms and combined with environmental variables to establish a Temperature-Latitude (TL) dataset. Sensitivity testing was also conducted to examine the roles of eveness/unevenness (structure) within the sample design, numbers of species and taxonomic resolution on the multi-variate analyses and model output. While latitude, salinity and phosphate were the variables that consistently explained the greatest proportion of variability across the different datasets, salinity, temperature and nutrients were dominant when latitude was removed. Most models using TL datasets improved reconstruction errors; however, the nested (nTL1) dataset provided the best inferred-temperature history for Wyee Bay when validated by long-term monitoring data. Generally, the environmental variables attributable to gradients between lakes were the same regardless of the number of species, sample design or taxonomic resolution.

To increase our understanding of the changes in diatoms and lake ecology over a greater pre-power station and pre-industrial (heavy metals) period two additional cores were obtained for the final phase of the study. At both a plume-effected and a control site cored sediments were analysed for heavy metals and ^{210}Pb to establish and cross validate geochemical chronology and identify pre-industrial boundaries. While only sediments of the Crangan Bay core were preserved adequately for dating it provided key information relative to the original Wyee Bay core. Prior to heavy metal enrichment in the southern lake (1925-1942), Crangan Bay (control) (20-42 cm) and Wyee Bay (pre-1935) supported a similar diatom flora. Thus, it was inferred that the environmental condition of the lake's southern embayments were likely to be similar at that time and relatively stable for Crangan Bay to at least ~1790.

The work described here demonstrated the applicability of benthic diatoms as tools for understanding spatial and temporal changes in a coastal lake associated with a power station thermal plume. Diatoms and the multi-taxa approach could be utilised as bioindicator-type tools for regular broadscale assessments of south-east coast estuarine health.

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Part 1

Chapter 1

Chapter 2

Introduction

1.1 Project Background

In 2001 the Waters and Coastal Science Section of the New South Wales (NSW) Environment Protection Authority (EPA - now the Office of Environment and Heritage (OEH)) commenced a program called the Point Source Project. The program was composed of a series of scoping studies investigating new qualitative and quantitative physio-chemical and bio-indicator-type approaches that could be applied for the more effective and sustainable management of the state's licensed coastal point source discharges. This PhD project arose as part the program and focused on the thermal discharge from Vales Point Power station, located on the shores of the state's largest coastal lake, Lake Macquarie. The study examined the potential for benthic diatoms to be used as a tool to better understand the effects of the artificially heated waters on the ecology of the receiving embayment and for bio-monitoring of plume extent effects.

The EPA's Point Source Project was finalised in 2005 (then called the Department of Environment and Conservation) and preliminary results from the diatom study were reported internally. Until recently the initial study and subsequent research, however, remained unpublished. This thesis details the expanded PhD project's outcomes presented as a series of chapters, scientific journal publications and appendices.

The work is novel in that it sampled for benthic diatoms using a replicated nested sampling design (multiple within site and within bay replicates) with impact and multiple control embayments to examine variability in assemblages over multiple spatial scales. It also examined those diatoms preserved over time within the sediments of the effected embayment as well as a control location. The acquisition of modern analogue reference datasets facilitated the development of diatom-models and temperature transfer functions to infer past estuarine conditions within the receiving water embayment. The work was multi-disciplinary in that a range of techniques were employed to better understand the interaction of the plume with the receiving environment. This included remote sensing techniques using thermal satellite imagery to determine the temporal and spatial variability of plume temperature and extent. Geochemical profiles of southern lake sediments were also determined with the analysis of heavy metal, organic matter, particle size and radio isotopes (Berrylium-7 (^{7}Be) and Lead-210 (^{210}Pb)) at key sites. These data provided an improved historical understanding of the exposure of the southern lake to a range of anthropogenic pressures.

The spatial variability of estuarine benthic diatom species along a latitudinal temperature gradient from southern Queensland - northern New South Wales to the Victorian border was also investigated. This provided a secondary reference dataset, used to develop an alternative diatom-inferred temperature model and test if model performance was improved. Some analysis was also performed on the variability in model output based on reference set size and taxonomic resolution. The analyses of more than 150 sediment samples during the course of the study has lead to a species catalogue and morphological data on >500 benthic diatom morphotypes for mud-dominated estuaries from south-eastern Australia (2002-2009). This dataset provides geographical range and relative abundance information for east coast Australian estuaries that, combined, have not been reported previously.

1.2 Pollution and environmental management

1.2.1 Anthropogenic pressures on environmental systems

Anthropogenic pressures were first placed on Australia's unique environments and its organisms with the arrival of humans on the continent some 60 ka years ago (Flannery, 1994). European settlement (c. 1788), immigration and more recently, modernisation of the economy, have driven population growth and associated rural, urban and industrial expansion across the country. These factors have provided a complex mosaic of new pressures upon environmental systems and the organisms living within them. For Australia, these pressures have mostly been concentrated within the coastal zone with all of our major cities and ~85 % of the population living within 50 km of the sea (State of the Environment, 2006). Pollution is one such pressure that arises from human activity and involves the release of a substance (or substances) into the environment as a bi-product of rural, industrial and/or urban practices or processes. The implications for the environment include degraded air and water quality as well as altered functioning and condition of ecological systems (Langford, 2001).

Pollution takes many forms but is generally classified by the way it enters the environment. When pollution enters the environment dispersed across an area and delivered to a waterbody indirectly it is termed a diffuse source (i.e. crop sprayed pesticides). Alternatively, where pollution is delivered directly via a pipe or channel, it is termed a point source (i.e. sewage outfall). Runoff from the site of an urban development after rain is considered, for example, a diffuse pollution source. In this case, the pollution may increase the nutrients and sediment load delivered to a waterway invoking eutrophication and algal blooms. An effluent discharged from a construction site pipe to an estuary, however, is a point source and may effect the receiving environment in several ways. The discharge may reduce oxygen concentrations in the water if it contained high levels of bacteria. The discharge may also contaminate bottom sediments if laden with heavy metals and/or smother benthic organisms with relatively high levels of suspended particulates. Similarly, the discharge of heated-water from a power station cooling tower to a coastal lake is a form of point-source pollution. In this case the temperature may alter the "natural" temperature regime of the receiving water body that in turn has implications for the ecology of the organisms living within it (Langford, 2001).

A shift in global climate is expected to have wide-ranging implications for the functioning of biological systems. In south-eastern Australia, the Tasman Sea is predicted to be one of the world's most rapidly warming regional seas (Cai et al., 2005), associated with strengthening flow of the East Australian Current (EAC) (Ridgway and Hill, 2009). This is likely to have implications for regional climate and coastal systems. Estuaries are unlikely to be immune to such fundamental system changes as the systems are intrinsically linked (Gillanders et al., 2011). Coastal inundation, geomorphological and catchment process changes as well as altered temperature, salinity and flow regimes are issues likely to have implications for estuaries and their organisms. Thus, in light of these changes, a re-assessment of the strategies for the management of pollution and anthropogenic disturbance in coastal systems is prudent.

Whole of system multi-disciplinary approaches are required to provide improved understanding of change in environmental systems over various spatial and temporal scales to manage the impacts on these systems into the future. Studies employing ecologically based multi-taxa and bio-indicator-type techniques, combined with catchment modelling, remote sensing and traditional water quality assessments provide a more holistic perspective of environmental condition than each technique alone.

1.2.2 Monitoring and assessment of aquatic system health

Historically, science has utilised the physical and chemical attributes of the water or sediments to gain an understanding of environmental variability within aquatic systems and provide a proxy to infer changes in system function. In more recent times, methods of measuring ecosystem function using organisms, termed bio-indicators, have been developed (Niemi, 2004) and their use is becoming more widespread. Organisms are ideal as indicators of system health as they describe the full effect of physical and chemical changes to an environment directly (Reid et al., 1995). Through quantitative approaches using manipulative experiments and hypothesis testing, these bio-indicators can not only provide an improved understanding of ecosystem function but can also be applied to environmental effect-type assessments (Underwood, 1998).

1.2.3 Pollution, phytoplankton, phytobenthos and benthic diatoms

In order for an organism or group of organisms to be effective bio-indicators the organisms must be sensitive to changes in both the biotic and abiotic environment and responses to these changes must be predictable (Reid et al., 1995). The application of bio-indicators in the assessment of the effects of point source pollution to aquatic systems has been reported widely. Studies focusing on point source thermal pollution have used multi-taxa approaches examining fish (Sandström 1990; Teixeria et al., 2009), water column plankton (Keskitalo 1987; Mallin et al., 1994; Jiang et al., 2009) macrophytes (Squires et al., 1979; Electricity

Commission (EC) of New South Wales 1983; Ralph 1998), and benthic infaunal communities (Powis and Robinson 1980; Bamber and Spencer 1984; Lardicci et al., 1999).

The use of benthic organisms is considered to be advantageous, when compared to relatively more mobile pelagic organisms, in that they provide a more temporal-spatially normalised expression of the environmental pressures at a sampling location (American Public Health Association, 1998). In Australia, diatoms and macro-invertebrates are two examples of groups of benthic organisms that have been employed as bio-indicators in freshwater systems (Chessman, 1995). Macro-invertebrate assemblages and diversity have been used to assess river health (Chessman, 1995) and combined with periphyton to examine effects of river system flow regulation (Growns and Growns, 2001). Macro-invertebrates were applied in preference to diatoms as the rapid assessment tool (Chessman et al., 1999) and are currently used by state and territory agencies as part of the Australian River Assessment System (AusRivAS) program (http://ausrivas.canberra.edu.au). For estuaries, the use of macro-invertebrates as general indicators of system health is limited. Studies have been limited in spatial extent and focused on distributions relative to heavy metal contamination in sediments of individual systems (Roberts et al., 1998: Simpson et al., 2005). Generally, the use of bio-indicators as broad scale assessment tools for Australian estuaries is relatively recent.

Elsewhere, diatoms have been used widely as environmental indicators. Benthic diatoms are particularly useful because they are abundant and cosmopolitan in nature, less habitat dependant than macro-invertebrates and possess a well studied taxonomy and ecology (Reid et al., 1995). Diatoms are sensitive to a range of environmental variables and have been applied across a range of disciplines including climatology, hydrology, geomorphology and biogeography. Studies attributing diatom distribution to regional, broad-scale patterns of temperature have been reported for oceanic systems (Crosta et al., 2005; Esper et al., 2010), Arctic freshwater lakes ((Weckström et al., 1997); Pientitz et al., 1995) as well as coastal lagoons (Facco and Sfriso, 2007). Diatoms have also been applied in water quality monitoring and point source pollution assessments. Studies investigating thermal point sources using periphytic or benthic microalgae have focused on discharges to rivers (Descy and Mouvet 1984; Vinsen and Rushforth 1988), lakes (Hickman 1974; Hickman and Clarer 1975), cooling ponds (Snoeijs and Prentice 1989) or within power station canals (Snoeijs 1991). Work examining the effects of nutrients from sewage discharges (Underwood et al., 1998; DelaCruz et al., 2005) using periphytic algae has also been reported.

,While the cosmopolitan nature and widespread abundance of organisms is often advocated as a necessity for a bio-indicator species (Hall and Smol, 1992), others consider that these features may make them unsuitable. Inertia in populations means that cosmopolitan species exhibit little or no response to environmental change and rarer species are likely to be better indicators of change (Underwood, 1989). More recent evidence, however, indicates that endemism and local adaptation to environmental conditions for benthic diatoms does exist (Vyverman et al., 2007; Vanormelingen et al., 2008).

Diatoms provide another advantage as a bio-indicator organism as their silica skeletons are relatively robust and are readily preserved in bottom sediments. These fossil diatoms can then be used to reconstruct past conditions using palaeolimnological techniques (Moser et al., 1996). For Australian systems, a range of biogenic elements preserved in sediments have been employed to determine a sediment chronology and infer pre-anthropogenic conditions of aquatic systems. Fossil pollen (McMinn, 1992), crustacean tests (Ralph et al., 2011), photosynthetic pigments (Hodgson et al., 1998), dinoflagellate cysts (McMinn et al., 2004) and diatoms (Tibby et al., 2003; Saunders et al., 2008; Logan et al., 2010) have been reported in the literature. For marine and estuarine environments, however, the use of benthic diatoms in palaeoecological studies is yet to reach its full potential (McMinn et al., 2004). While palaeoecological techniques are applied as a management technique in the USA, their broadscale application for determining reference conditions for Australian estuarine ecosystems is yet to be realised (Saunders and Taffs, 2009).

1.3 Benthic Diatoms

1.3.1 Biology and Ecology

Diatoms are a diverse group of unicellular, eukaryotic algae that are key components of most aquatic systems and can be found in ice, soil and other moist environments (Tomas, 1999 cited in Round et al., 1990). They are predominantly autotrophic and distinct from other groups of algae in that they possess a cell wall impregnated with silica to form a rigid skeleton. The skeleton itself is often highly differentiated and it is this morphology, backed up with molecular methods, that provides the basis for diatom taxonomy and phylogeny.

Diatoms are common to marine, estuarine and freshwater systems. While many species live free and unattached within the water column as part of the plankton, a distinctive group of species live within or on the surface of sediments, rocks, plants, animals or other substrata. These benthic species live either attached to the substrate or as unattached motile cells within the sediment surface layer. Together, these diatoms form a significant component of the wider microscopic benthic flora termed the microphtyobenthos. The pervasive and cosmopolitan nature of the diatoms, but responsive biology makes them ideal organisms for investigation of responses of systems to environmental pressures. Examples of species identified from sediments of south-east Australian estuaries are presented in Figure 1.1.

Diatoms are abundant in almost all aquatic habitats and make up a large proportion of the phytoplankton and phytobenthos within freshwater and marine environments. While planktonic diatoms have been studied widely and much about their ecology has been reported, the ecology of benthic diatoms is relatively less well understood. This is due, in part, to difficulties associated with sampling and quantifying them (Round et al., 1990). For planktonic forms living suspended within the water column, the availability of nutrients and cell density are the most important factors influencing growth and behaviour. For benthic diatoms, however, buoyancy is not an issue and nutrients are in ample supply. The environment they inhabit is relatively two-dimensional in that benthic species exist within a

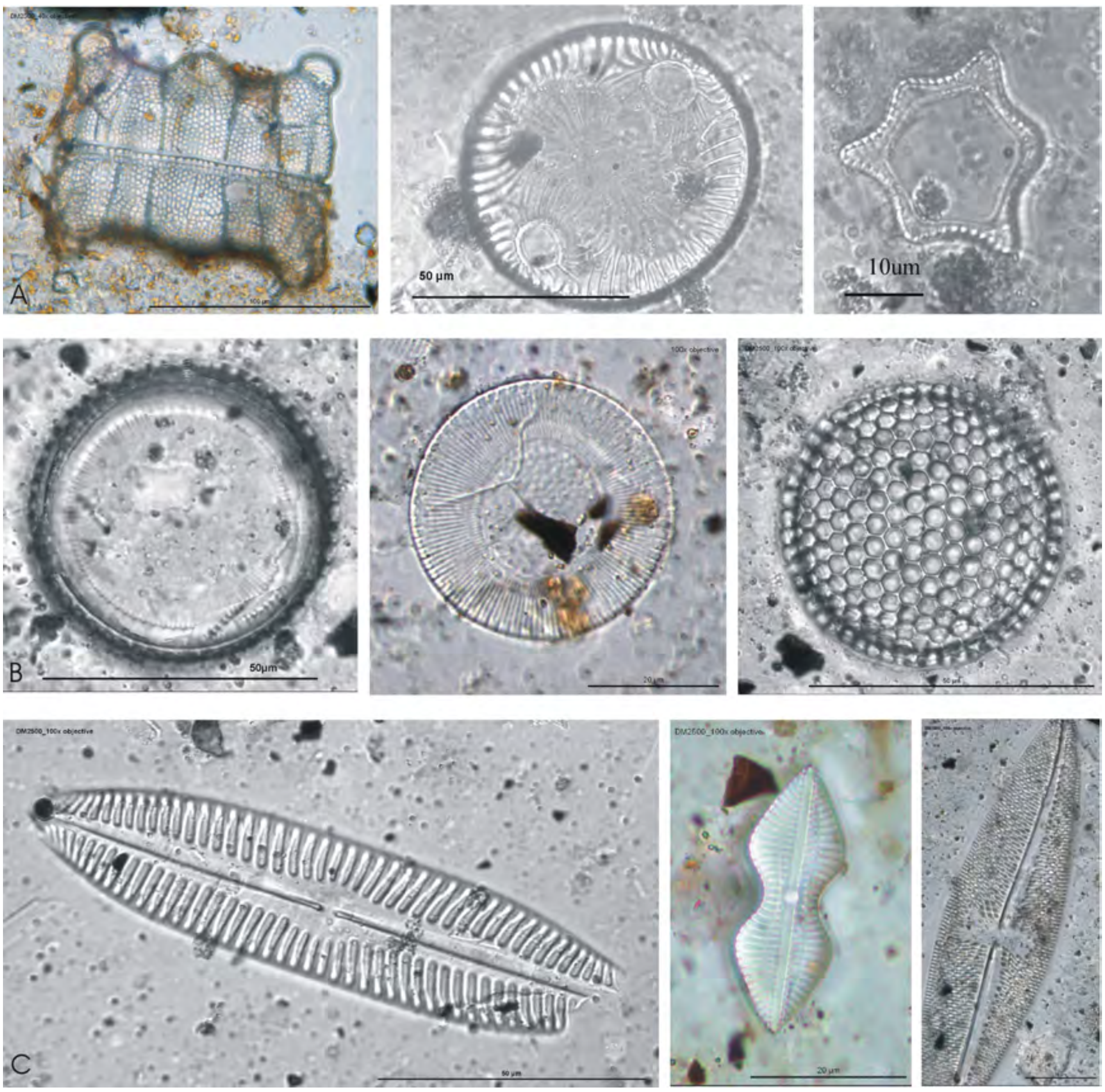

Figure 1.1 Photomicrographs of species of the Bacillariophyta; left to right **A**. bi-polar to multi-polar centric diatoms of the Mediophyceae from left to right *Biddulphia pulchella* Gray, *Auliscus sculptus* (W Smith) Ralphs in Pritchard and *Triceratium dubium* Brightwell; **B**. single-pole centric diatoms of the Coscinodiscophyceae - *Melosira sulcata* (Ehrenberg) Kutz var. *radiata* Grunow, *Cyclotella striata* (Kutzing) Grunow, *Stephanopyxis turris* (Greville) Ralphs; and, **C**. bi-laterally symmetrical pennate diatoms of the Bacillariophyceae – *Navicula yarrensis* Grunow, *Diploneis* sp. and *Trachyneis aspera* (Ehrenberg) Cleve.

thin layer of oxidised sediment constrained by the water above and substrate below. As part of this habitat, benthic diatoms must contend with factors such as burial, grazing, bioturbation and/or resuspension.

1.3.2 Diatoms and the estuarine environment

Together, planktonic and benthic microalgae may contribute to up to 70% of the primary production within aquatic systems (McMinn et al., 2004) or up to 50% of primary production for estuaries (Kromkamp et al., 2006). Benthic algal communities are not pure diatom assemblages but consist of several microalgal groups (including benthic cyanobacteria and other green algae) that together are termed the metaphyton (Behre, 1956 in Round et al., 1990), benthic microalgae (BMA) or microphytobenthos (MPB) (Kromkamp et al., 2006). Generally, the MPB plays a key role in an aquatic system, in that it provides a supply of organic matter and controls nutrient fluxes between the sediment and the water column (Kromkamp et al., 2006). The diatoms, however, often constitute a significant and dominant component of the MPB in coastal estuarine systems (Sullivan, 1999). More specifically, the floral composition of the diatoms can be a controlling factor in the functioning of the sediment biofilm and estuarine nutrient cycling (Underwood, 2005).

While diatoms may exert some influence on their environment, the environment also acts as a control governing aspects of diatom ecology. Diatoms are sensitive to changes in the aquatic environment with changes in salinity or temperature regimes, for example, invoking changes in diatom abundance and/or assemblages. External factors may also act at a more fundamental and cellular level, altering diatom morphologies and or cell chemical processes. Changes to pore size and cell wall thickness of *Cocconeis placentula* has been observed in response to fluctuating salinities in the Coorong (South Australia), likely as a means of regulating cell nutrient uptake (Leterme et al., 2010). Similarly, temperature is a controlling factor for cell size and stoichiochemistry (Finkel et al., 2010). Changes to diatom structure and function, may alter assemblages that in turn may have implications for food web dynamics (Finkel et al., 2010).

In the case of temperature, the discharge of cooling water from a power station, is likely to result in an alteration of the natural temperature regimes of the receiving water body. Previous studies have identified decreases in the photosynthetic efficiency and productivity of epiphytic algae (Hickman and Klarer 1975; Chaung et al., 2009), altered patterns of dominance (Anraku, 1974) and/or a reduction in species diversity (Hein and Koppen, 1979) within the receiving environment. Changes in species abundance (Rajadurai et al., 2005) and/or increased standing crop size but not necessarily species composition (Hickman, 1974) were also observed in response to a thermal plume. Thermal discharges also promote invasive species (Thomas et al., 1986). All these changes can, in turn, invoke ecosystem-wide alterations with top-down and bottom-up effects (Mallin et al., 1994).

1.4 Palaeoecology

1.4.1 Diatom Models and Transfer Functions

Diatom-based models and the use of transfer functions for inferring past environmental conditions for south-east Australian systems have mainly focused upon freshwater systems. Models have been developed for evaluating historical changes in electrical conductivity in river connected wetlands (Tibby et al., 2007) and phosphorus in water storages (Tibby and Reid, 2004) within the Murray-Darling basin. The application of these techniques in relatively shallow-water (<5m) coastal environments has been considered problematic and thus has been underutilised in estuarine systems (McMinn et al., 2004). Factors such as bioturbation and reworking of sediments by wind-induced wave action can disturb sediment layering and disrupt chronologies (Eisma et al., 1989). Despite these factors, recent studies have developed transfer functions for phosphorus in the Richmond River estuary (Logan et al., 2011), salinity in brackish East Gippsland lakes (Saunders et al., 2008) and eastern Victorian-Tasmanian estuaries (Saunders, 2010). The body of work has demonstrated that where sediment stratigraphic integrity has been adequately preserved, palaeoecological techniques can be applied to estuaries for the reconstruction of past environmental trends. Similarly, since palaeoecological techniques have been used to examine decadal to century scale changes in climate (Fritz et al., 1991; Tibby and Tiller, 2007) these may also be successfully applied to estuarine environments.

1.5 Physical Setting

Lake Macquarie is a coastal barrier lake located approximately 80 km north of Sydney on the NSW Central Coast (Figure 1.2) that formed at the end of the last inter-glacial transgression, approximately 12 ka years ago (Roy and Peat, 1975). Similar to many other south-east Australian estuaries, Lake Macquarie is a back barrier (Roy et al., 1980) or wave-dominated estuary (Digby et al., 1999), formed as the result of a wave-built sand barrier across the seaward end of one or several small river valleys.

The lake has been relatively heavily impacted upon by large urban and industrial development (Roy and Crawford, 1984) including a Lead-Zinc smelter in the north of the lake at Cockle Creek (1890-1995), coal mines and discharges from sewage treatment plants. Several power stations have also been constructed on the banks of the lake due to the proximity of coal reserves and the availability of water for cooling generator turbines. Ash dams receiving the ash waste from the power stations also lie adjacent to the lake, the runoff from which has in the past contributed heavy metals including selenium to lake waters and sediments (AWACS, 1995). Wangi Wangi was the first power station to be constructed (1956) followed by the commissioning of Vales Point (1963) and Eraring (1982). Only the latter two stations remain in operation today. Water taken from the lake is utilised to cool steam condensers that is then released back to the lake where it mixes with ambient lake water.

1.5.1 Pre-Quaternary Geology

Bedrock strata in and around Lake Macquarie are comprised of Triassic sediments conformably overlying Permian sedimentary sequences. Both sets of strata dip to the south and form the northern section of the Sydney Basin (Roy and Peat, 1973). Permian rocks outcrop to the north and east of the lake and are composed of sandstone, conglomerate, tuff and coal. These coal seams are broadly divided into two structural groups termed the Newcastle and Tomago Coal Measures. Younger Triassic rocks outcrop around the south and southwest margins of the lake and are composed of sandstone and conglomerate of the Munmorah Conglomerate. This stratigraphic unit forms the basal unit of the Narrabeen Group that also contains both the Hawkesbury and Narrabeen sandstones characteristic of the Sydney basin coastline.

1.5.2 Quaternary – Pleistocene and Holocene

Approximately 18 ka years ago at the end of the Pleistocene seas along the east coast of Australia began to rise marking the end of the glacial period and the start of the Holocene glacial-interglacial transgression. Sea level stabilised between 12-6 ka years ago so that, with an abundant nearshore sand supply, resulted in an accreting or stable coastline that has persisted for at least the last 4000 years (Thom, 1975). The formation of many NSW and Victorian estuaries, including the relatively shallow coastal lakes and lagoons, resulted from the impoundment of bodies of water against the coast behind a seaward barrier of marine sand (Roy et al., 1980).

Late Pleistocene and Holocene coastal sand barriers lying between bedrock headlands characterise the coastal margin of the south-east Australian continent. This section of coast is exposed to a high-energy wave climate dominated by south-easterly swells generated from within the Tasman Sea (Thom et al., 1973,). While sea level has remained relatively stable, the NSW coastline has experienced significant changes to sand supply and coastal conditions over the past 3000 years (Roy and Crawford, 1977).

The oblique orientation of the coast relative to the wave climate results in littoral drift and the net transport of nearshore sediments from south to north (Delft, 1970; Roy et al., 1980). Sand from the NSW coast ultimately ends up in large sand complexes offshore of south-east Queensland and includes the large sand islands characteristic of this section of coast. Sand lying on the continental shelf or at depth may then be periodically delivered to the adjacent abyssal plain by turbidite flows (Boyd et al., 2008). Overall, sediment budgets indicate that the delivery of sands from catchments to the coast by NSW rivers are not significant enough to compensate for the loss from ocean beaches due to northward littoral drift (Roy and Crawford, 1977).

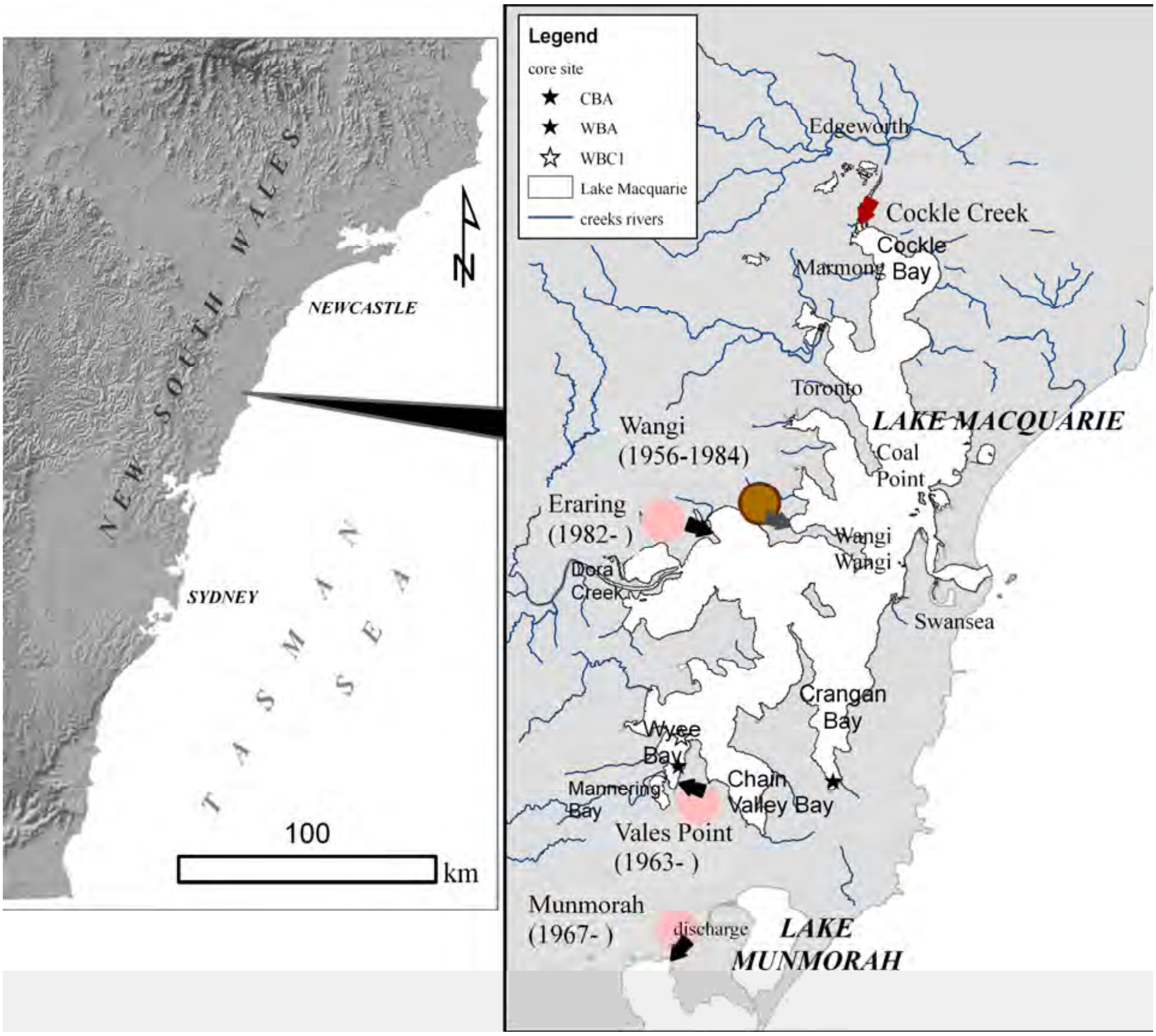

Figure 1.2 Location of Lake Macquarie on the New South Wales Central Coast and power stations operated since 1956.

1.5.3 Ocean and climate

The coast of south-eastern Australia is dominated by a temperate climate (26–43 °S) subject to inter-annual cycles of extended dry and wet periods associated with El Niño Southern Oscillation (ENSO) (Powers et al., 1999) and the Southern Annular Mode (SAM)

(Cai et al., 2005). Mean total monthly rainfall is around 70-90 mm (Australian Bureau of Meterology (BOM) data Wyee Station 61082 for 1910-2003) and monthly mean daily maximum air temperature (BOM Nobbys Head, Newcastle station 61055; 1910-2003) ranges from a minimum of 16.8 °C in July and maximum of 25.0 °C in January-February.

The coastal ocean within the region is dominated by the flow and seasonality of the East Australian Current (EAC) (Ridgway and Hill, 2009). The EAC peak flow occurs in the austral-spring summer reaching speeds on average of between 1-2 knots (at 34° S Port Hacking, Sydney) with variation in inter-annual net flow of between 5-16 Sv (Ridgeway et al., 2008). EAC surface temperatures off the NSW coast generally range between 17-24 °C with episodic upwelling of colder (<15 °C), nutrient-rich shelf water driven against the shore and into the photic zone during spring-summer.

1.5.4 Lake Morphology, Hydrology and Sedimentology

A geomorphological classification scheme and summary of the key features of Australia's estuaries is provided on the OzCoasts website (www.ozcoasts.org.au) and condition of estuaries provided in National Land and Water Resource Audit (2002). Generally, the sedimentology of estuarine lakes and lagoons of NSW can be characterised by relatively small fluvial sand and mud deltas adjacent to creeks and tributary inputs, mud basins in broad and relatively deeper areas and shallow sandy flood/ebb tide deltas of marine sands and associated with the entrance and lower estuary. Creeks and rivers draining to the coastal zone in the vicinity of Lake Macquarie are relatively small and deliver insufficient quantities of terrestrial sediments to infill the coastal valleys (Roy and Crawford, 1977).

Lake Macquarie is the largest coastal estuarine lake in NSW, covering a surface area of more than 114 km^2 with a catchment area of 786 km^2. The lake runs parallel to the coastline in a northeast-southwest orientation reaching up to ~ 22 km long and 10 km wide. Three major embayments characterise the southern end of the lake that, from east to west, are known as Crangan Bay, Chain Valley Bay and Wyee Bay (Figure 1.2). Crangan Bay is the eastern-most embayment with the most undeveloped catchment. The embayment is often utilised as a control location for environmental studies as it is fringed by native bushland with urban development restricted to several isolated settlements such as that of Nord's Wharf and Gwandalan.

Further west the Vales Point Power station straddles the Mannering Park peninsula and lies on the shores of both Chain Valley Bay and Wyee Bay. The power station draws water from the lake via an intake channel midway along the western shore of Chain Valley Bay and discharges it from a canal into shallow waters (<1m) at the southern end of Wyee Bay. Small creeks enter each embayment at or close to the southern end of each of these embayments. In Wyee Bay, Wyee Creek drains the catchments to the west while Mannering Bay, lying downstream and to the north of the 'ash-dam' area known as Mannering Lake, that together both discharge along the bay's south-western shore.

The tidal channel entrance, located near the township of Swansea, ranges from 200-400 m wide along its 3.5 km length (AWACS, 1995). The narrow entrance relative to lake size severely restricts tidal exchange to <1% per tidal cycle (Spencer, 1959) with a tidal range at the entrance in the order or 1.5 m reduced to 0.06 m within the upper most parts of the estuary (Stone, 1964 cited in Roy and Peat, 1976). Despite the limited tidal exchange, the estuary is pre-dominantly marine with relatively small freshwater inflow from the catchment. The largest potential sources of freshwater are from Cockle Creek in the north and Dora Creek to the west. Shallows located between Swansea and Wangi Wangi divide the lake and restrict water movement within deeper sections of the lake into two separate zones and circulation in upper embayments is driven by locally generated wind waves (<1m) (Spencer 1959; WBM Oceanics 1997).

Like many of south-east Australia's estuaries, the evolution of the coast has facilitated the preservation of a sedimentary sequence ideal for environmental studies (Nichol, 2001) and attributes of Lake Macquarie make it an ideal candidate for palaeolimnological-type investigations. The lake is a low energy mud basin that receives a limited sediment load via the relatively small creeks and catchments (Roy and Peat, 1975). Lake sediments are predominantly estuarine mud, in ample supply, delivered from creeks from the heads of many of the lakes embayments (Roy and Peat, 1975). Muds form a mantle of sediments, unconformably overlying older Permian and Triassic rocks, on the lakebed with the sides of embayments grading to sandy mud and muddy sand with a decrease in water depth (Roy et al., 1981). Lake depth and restricted tidal exchange function so that after periods of heavy rainfall sediment is generally retained within the lake basin and not lost to the ocean. The fine (<63 μm) terrigenous sediment is delivered from the catchment by creeks and rivers which then settles from suspension in the low energy environment of the lake basin (Roy and Peat, 1975).

Sands are either fluvial in origin, expressed as small deltas at the entrances of small creeks and rivulets, clean quartzose marine sands associated with the entrance and prograding flood tide delta, or reworkings of weathered Pleistocene marine sands along the lake's mid to upper shores (Roy et al., 1980). Most of the lake bed is below effective wave base limiting sediment resuspension (Roy and Crawford, 1984).

Lake Macquarie sediments describe a relatively continuous record of Holocene deposition with sedimentation commencing approximately 7500 years ago (Roy and Crawford, 1984) with a shallowing of the lake since sea level stabilised 6000 years ago (Thom and Chappell, 1975). In Lake Macquarie sediments extend to 21.5 m below sea level and are up to 12 m thick (Roy et al., 1980). Stable hydrodynamic conditions have prevailed in the lake for at least 1000 years, indicated by the homogeneity of the upper section of the mud sequence (Roy, 1981). Sedimentation rates determined from fossil shell assemblages were calculated as 0.17- 0.86 mm $year^{-1}$ specifically 0.4-0.6 mm $year^{-1}$ for southern embayments (Roy et al., 1980). As these rates were calculated over 1000's of years, the accuracy of these estimates were questionable according to Batley (1987) who determined sedimentation rates from more recent sediments (<200 years) by dating heavy metal horizons indicating sedimentation rates in the order of 1.1-5.7 mm $year^{-1}$.

Upper sections of cores from deeper sections of the lake are mud dominated reflecting the relatively low energy depositional environment. Muddy sediments are often interrupted by the presence of a distinct shelly horizon at depth (Roy, 1981) . The shell component of sediment is generally relatively low in the top 10-20 cm of sediment but increases below this zone. The low energy environment suggests that shells are allochthonous and are not likely to have been transported from elsewhere in the lake. Shells are predominantly whole or fragmented specimens of the genera *Notospisula* and *Anadara* present in soft sediment habitats across the lake. While *Notospisula* is considered to be relatively rare, *Anadara* is commonly found living amongst sea grass beds of *Zoestra* and at water depths of less than 2-3 m. *Pyrazus,* a genera commonly associated with *Anadara* within Lake Macquarie sea grass beds, is absent from the sediment record (Roy, 1981). The feature likely indicates a change to the depth distribution of benthic infaunal species at these sites within the lake. Most importantly the horizon indicates a change in the regime of bioturbation after this time with implications for the sediment chronology in these areas.

1.5.5 Industrialisation and urban development

The lake has been relatively heavily impacted by large urban and industrial development (Roy and Crawford, 1984) and the lake and its catchment are generally considered to be highly modified (NLWRA, 2002). Physical alteration of the catchments through land use changes, generally, contribute to changes in hydrological regimes and ultimately the loads of diffuse pollutants delivered to waterways (Harris, 2001). The north, west and north-east areas of Lake Macquarie are relatively highly urbanised with the suburbs of Newcastle occupying broad areas of these sub-catchments and encroaching onto the foreshore (Figure 1.2). In the west, urban development is interspersed with rural areas and bounded by areas of State Forests and National Park in upper catchments. By comparison the south and south-eastern sections of the lake are relatively underdeveloped with isolated townships, national park, nature reserves and state recreation areas.

Historically, point sources have been a major contributor of pollutants to the lake. A lead-zinc smelter (1897-1995) in the north of the lake near Cockle Creek discharged industrial wastes and was identified as the source for the widespread enrichment of lead, zinc, cadmium and copper in the lake sediments (Roy and Crawford, 1983; Roach et al., 1995; Olmos and

Birch, 2010). Power station ash dams that receive the ash waste from the burning of bituminous coal also lie adjacent to and within the catchments of the lake. Runoff from these dams in the past has contributed heavy metals including selenium to lake waters and sediments (AWACS, 1995; Peters et al., 1999a; 1999b). The relatively recent introduction of filtering for power station stack emissions (2006) may have facilitated a decrease in airborne metal contributions to lake waters (Scrivener, pers. comm.). A decrease in metal concentrations for the lake in general in recent years is likely to reflect tighter controls on the discharge of these pollutants (Roach, 1995).

Secondary treated sewage discharged to the lake from Sewage Treatment Plants (STPs) at Toronto, Edgeworth and Marmong contributed nutrients and other pollutants to the lake. Loads of 57.3 tonnes year^{-1} nitrogen and at 30.5 tonnes year^{-1} phosphorus were being delivered to the lake at a rate of 13.5 ML.day^{-1} in 1983 (AWACS, 1995). While phosphate reduction technology introduced at Toronto STP in 1989 may have contributed toward a decrease in lake water phosphate concentrations, Toronto STP only accounted for only 20% of the sewage volume and 14% of the phosphorus load to the lake at the time (AWACS, 1995). The majority of sewage discharges to the lake were redirected to the ocean during 1992-94 (Hunter Water, pers. comm.) with the construction of an outfall at Belmont (dry weather flow ~ 25 ML day^{-1}). With the cessation of discharge at Cockle Creek from West Wallsend STP in 1997 effluent no longer entered the lake directly under dry weather flows (AWACS, 1995).

The gradual decline in sewage input is reflected in the distinct decline in the average concentrations of nutrients within lake waters in the mid 1990s (Eyre, 2005). Additionally, improved storm water and land management practices may have contributed to the decline in mean nutrient concentrations to 2005 (Eyre, 2005). A total of 360 tonnes year^{-1} of nitrogen and 23 tonnes year^{-1} of phosphorus are estimated to be delivered to Lake Macquarie from its catchment from urban, rural and natural areas (NSW Water Board, 1992 cited in AWACS, 1995).

Three power stations have operated on the shores of Lake Macquarie since 1956 using lake water to cool steam condensers then releasing it back to the lake to mix with ambient lake water. Vales Point (1963) and Eraring (1982) remain in operation today and discharge a combined instantaneous flow of ~130 m^3s^{-1} (NSW OEH Licence Annual Returns, 2008). The thermal discharges from the power stations are significant contributors to basal load temperatures and the heat budget of the lake (Floyd, pers. comm.). Environmental protection licence agreements between the operators and state agencies (Protection of the Environment Operations (POEO) Act currently administered by NSW OEH) limit the maximum temperature and daily volume of heated water that can be discharged to the lake from the power station canals.

1.5.6 Vales Point Power Station

1.5.6.1 Operation

Construction of power stations on the NSW central coast commenced in the 1950s due to the proximity of coal reserves and access to water bodies that could be utilised as sources and sinks for turbine cooling water. Vales Point Power Station lies on the shores of south-western Lake Macquarie and was commissioned in 1963. The initial 600 MW capacity has been upgraded several times with commissioning of additional turbines to increase capacity to 875MW in 1966 and a second plant, station B, in 1978 increasing capacity to 2195 MW. Since 1989 the station has operated at a reduced capacity of 1320 MW following the replacement of the original turbines. The station uses lake water drawn in from Chain Valley Bay to cool its turbines and then discharges the water back into the lake at the southern end of Wyee Bay with a licensed discharge maximum temperature of 35 °C with limited release to 37.5 °C (NSW OEH Protection Of the Environment Operations (POEO) act Licence 761). Current license conditions limit the 35 °C threshold to be exceeded for the equivalent of 1.5 % of a day (21min 36s) and an additional 69 hrs a year (equivalent 11min 47s per day).

1.5.6.2 Power station discharge and the cooling-water plume

Cooling field surveys and modelling conducted in the early 1980s (ECNSW, 1983) describe elevated temperatures 5-7 °C above ambient between Vales Point and Wyee Point and 1-2 °C above ambient across the entrance to Chain Valley Bay and as far east as Pelican Rock. An area of 8.6 km^2 or equivalent of 6% of the lake surface area is affected by the Vales Point station cooling plume with a surface temperature elevation of >2 °C. Early field data indicated that thermal pollution from the power station discharges resulted in a "slight" elevation of temperature within the southern sections of the lake but that major changes to biological characteristics of the lake were unlikely (SPCC, 1983). More recent and comprehensive modelling exercises and data collection (AWACS, 1995) have provided similar cooling field extents with an improved understanding of three-dimensional plume behaviour. Remote sensing-type applications are currently in use for monitoring seagrass extent in response to the thermal discharges (T. Glasby, pers. comm.), however, monitoring of plume intensity and extent using techniques that assess thermal satellite imagery (Figure 1.3) are yet to be fully investigated and exploited.

Full monitoring and licence conditions tabled in the POEO license are detailed in Table 1.1 A series of other chemicals are added into the cooling water that is eventually discharged from the canal into Wyee Bay include:

- Antifoaming agents DEAIREX 8042 or 7055 up to 1680 $Lday^{-1}$ to control discharge of foam from the outlet canal.
- Biocide C-treat added to auxiliary and main cooling water circuits - no volume limits.
- Chlorination up to 1200 kg day^{-1}.

Loads based licence limits are also placed on salt, selenium and total suspended solids (TSS) but any limitation on allowable loads are not provided within the public license document attainable from the OEH website (http://www.environment.nsw.gov.au).

1.5.4 Environmental studies and monitoring

There are numerous studies of the effects of power stations on the coastal lakes of the NSW central coast. Combined with studies of other pollution sources and/or general lake wide water quality monitoring, Lake Macquarie has been studied more thoroughly than most other south-east Australian estuaries. Reviews of monitoring effort, summarising the apparent effects of the cooling water plumes on lake biota, generally concluded that “impacts” were localised and regionally insignificant (NSWEC, 1983; SPCC, 1983; AWACS, 1995). Changes to the composition and distribution of seagrasses in shallow areas near discharge points were identified and attributed to thermal pollution (EC 1983; SPCC, 1983) as were changes to abundances of invertebrates (Robinson,1982), mussels (Wallis, 1976), fouling organisms and gastropods (Bayliss, 1973) were also attributed to the thermal plume. Later studies focused on of the concentrations of heavy metals and the effects of metals entering the food web (e.g. selenium in Peters et al., 1999a).

1.5.4.1 Zooplankton

Kott (1955) conducted the first investigations of zooplankton in Lake Macquarie and described a seasonal succession of species. Further zooplankton work has been conducted as monitoring by the various power station operators (1975-) and limited to reports of total zooplankton counts. An analysis of zooplankton monitoring data (1975-1982) using a two-way analysis of variance indicated statistically significant differences in mean total zooplankton densities between plume effected and non-plume locations during spring and winter but not summer (NSWEC, 1983). Despite the result the authors argued that the effects of the thermal plume upon lake zooplankton populations were not likely to be significant as effects of temperature were expected to be greatest in summer. Regardless, effects on zooplankton populations were restricted to the southern section of the lake according to the authors and were small and localised (NSWEC, 1983; SPCC, 1983).

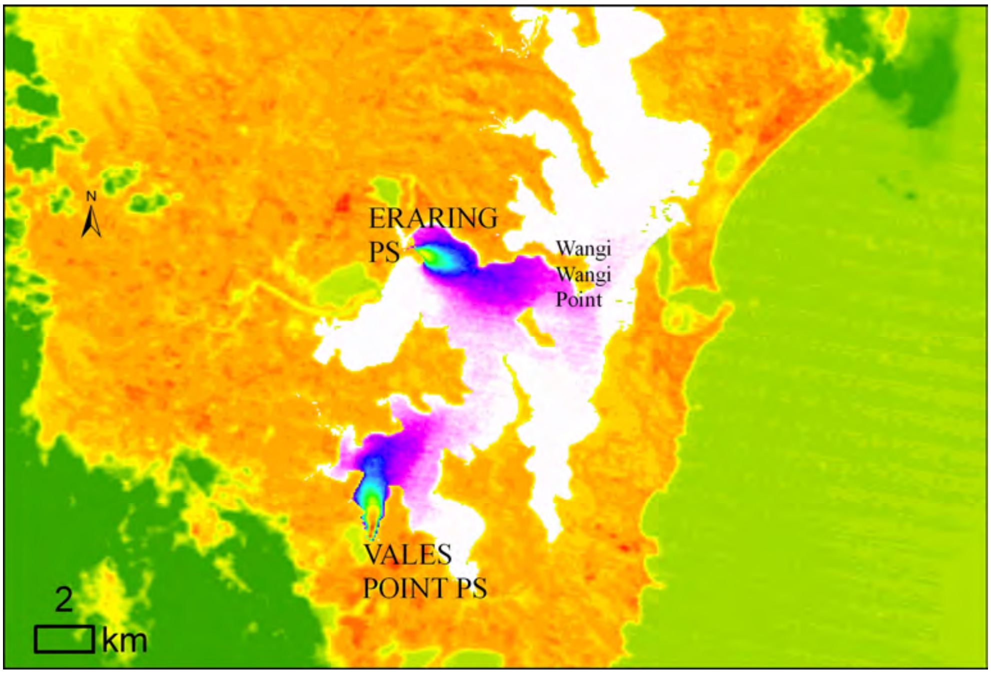

Figure 1.3 False colour United States Geological Survey Landsat 5 – Thermal Band 6 satellite image, 23 September 2003. Image overlaid Lake Macquarie median winter surface water temperature 2003-2008 denoting power station cooling water plumes.

Table 1.1 NSW Environment Protection Authority, Protection of the Environment Operations Act licence 761 with Delta Energy Vales Point Power station 2010.

Monitoring Point	**Monitoring type and location**	**98.5% Limit**	**100% limit**	**Discharge Volume Limit**	**Monitoring**
1	Temperature and volume cooling water outlet to Wyee Bay	temp 35 ºC daily (+ add. 69 hrs year^{-1})	temp 37.5 ºC Chlorine 0.2 mg L^{-1}	6500 ML day^{-1}	temp, oil and grease + daily discharge volume
2	Water quality monitoring ash water recycle system to outlet canal		pH 6.5 – 9.5 total suspended solids (TSS) 50 µg L^{-1}	120 ML day^{-1}	Cd, Cu, Pb, Mn, NO_2, NO_3, Total P, PO_4, Se, TSS, Zn, pH + continuous discharge volume
3	Non detailed monitoring of ash dam effluent application			380 kL day^{-1}	
4	Ash dam wall seepage		TSS 50 µg L^{-1}	500 kL day^{-1}	Cd, Cu, Pb, Mn, NO_2, NO_3, Total P, PO_4, Se, TSS, Zn, pH + continuous discharge volume
6	water quality at southern lake control location B5 10 times year^{-1}				Dissolved Oxygen, temp, salinity, water clarity (secchi), zooplankton (total counts)
7	water quality site B7 Wyee Bay 10 times year^{-1}				Dissolved Oxygen, temp, salinity, water clarity (secchi), zooplankton (total counts)
8	water quality near cooling inlet site LM15 10 times year^{-1}				Dissolved Oxygen, temp, salinity, water clarity (secchi), zooplankton (total counts)

Trend analysis of a longer-term (1975-1991) and higher taxonomical resolution dataset examined 16 species at 7 sites and identified a decline in taxa since monitoring began (MacIntyre and Holliday, 1993). While zooplankton population densities in the northern lake were considered variable, the southern lake was distinguished by relatively lower population densities. The structure of the communities were considered to be influenced by thermal effects from power station discharges south of Fishery Point (SPCC, 1983). A more recent study focusing on zooplankton within the lake's seagrass beds found the greatest diversity amongst seagrass beds of *Zoestra capricorni* (AWACS, 1995).

Current monitoring of the effects of the Vales Point discharge on water column biology is limited to the analysis of total zooplankton at 3 sites 10 times year^{-1}. Generally, analyses of total organisms or total plankton biomass are not considered to be good indicators of change (Beaugrand, 2004) in planktonic systems. Without detailed species level information current monitoring may be considered inadequate in its ability to detect critical assemblage changes resulting from effects from thermal power station discharges.

1.5.4.2 Seagrass and Benthos

While the first seagrass surveys of Lake Macquarie were conducted prior to power station commissioning in the 1950s (Wood, 1959) subsequent surveys were not performed until the 1980s. From the 1980s surveys have occurred at regular intervals, however, using a range of methodologies. This has made temporal comparisons difficult and resulted in conflicting conclusions in successive reports (SPCC, 1983; King and Hodgson, 1986; Winnings 1990; Hundley 1994 in AWACS 1995).

An overall decrease in seagrass coverage within Lake Macquarie, to the 1980s, was attributed to a decline in lake water quality associated with increased turbidity, chlorophyll levels and system eutrophication (Winning, 1990). On a smaller spatial scale, the complete or partial loss of *Zostera* at sites adjacent to power station discharges has been reported by several authors (SPCC, 1983; Gutteridge et al., 1992). In Wyee Bay the effects of temperature and turbidity associated with the Vales Point power station discharge were identified as responsible for a decreased abundance of seagrasses, decrease in observed depth range and a decrease in the spatial extent of *Zostera capricorni* and its replacement with *Halophila ovalis* (Barclay, 1978; Robinson, 1982). The implications for the removal of *Zostera* and/or its replacement with *Halophila* may be a reduction in habitat complexity (Hovel and Lipcius, 2002 in Cummins, et al. 2009) and a decrease in zooplankton abundance and diversity (Hundley, 1994 in AWACS, 1995).

Recent technological developments have seen seagrass surveying in Lake Macquarie move toward the use of remote sensing techniques. Currently, mapping occurs using low-altitude, high resolution (LAHR) aerial photogrammetry (NSW Department of Industry and Investment, Glasby, pers. comm.) coupled with field-verification (Cummins et al., 2009). This provides for rapid and robust assessment of temporal changes in seagrass health and distribution in the lake.

The most recent work, involving seagrasses, conducted laboratory based thermal tolerance experiments on species native to Lake Macquarie and other central coast lakes. A thermal exposure range of 15-30 °C was determined for *Halophila ovalis* (Ralph, 2008) and an upper limit of 31 °C for *Zostera capricorni* (Holland, 1982). *Zostera* was found to not recover when exposed to temperatures pulses >5 ºC or sustained temperatures of >30 ºC. Additionally, the growth of *Zostera* was affected in winter when temperatures exceeded 28 ºC (Ralph et al., 2009).

Surveys of the benthic infauna of Lake Macquarie were first conducted in the 1950s. McIntyre (1959) collected sediment samples and analysed the benthic infauna from over 400 sites within the lake to describe the broad distribution of infaunal species. The spatial distribution of benthic species were divided into four broad bio-physical categories termed entrance, slope, weed and mud zones.

The effects of power station discharges on infaunal benthos distribution follow a spatial pattern similar to that reported for seagrasses (Powis, 1973; Powis and Robinson 1980; Robinson, 1982). Studies concluded that the buoyant water plume impacted most significantly upon benthic assemblages in shallow water areas (<2 m water depth) adjacent to the discharge outlets but not on deeper water assemblages. Encrusting organisms were affected by the thermal plume from Vales Point with a reduction in abundance or elimination of sessile invertebrate species in areas where water temperature exceeded 5 °C above ambient (Bayliss, 1973). The complete extinction of the benthos adjacent to the Vales outfall and extensive modification to other communities further afield (in Wyee Bay) followed commissioning of Station B in 1978-79 (Robinson, 1982). Populations of species of shallow-water gastropods in Wyee Bay increased while populations of large bivalve species declined. Gutteridge et al., (1992) indicated that while abundance and diversity of benthic fauna was significantly less for Wyee Bay compared to control sites, the Wyee Bay site supported the greatest number of individuals of the bivalve *Theora fragilis.* Abundances were also relatively high for the bivalve *Cerithium coralium* otherwise absent when compared to all other lake sites.

1.5.4.3 Fish

An increase in the number of fish species during winter and decreased numbers, during summer have been observed in the area adjacent to the discharge point of the nearby Munmorah Power Station (New South Wales State Fisheries (NSWSF), 1980). Fish studies concluded that high thermal tolerance of some species and the active avoidance of high temperature areas by others, are responsible for the historically low or zero incidence of fish kills associated with power station discharges. Thus, the impact on fisheries was perceived to be negligible (ECNSW, 1983).

Commercial Fish Catch statistics (NSWSF, 1981) within Lake Macquarie suggest no decline in total catch or catch of dominant species since commencement of power station operations. A study of fish communities associated with the lake's seagrass beds, however, attributed changes in species diversity adjacent to Wangi Power Station outlet compared to control locations to temperature fluctuations (Friedlander, 1980). Scanes (1988) determined that, while some species decreased at discharge compared to control locations, generally greater numbers of fish were observed at Vales Point discharge site. A negative correlation between numbers of fish species and water temperature was observed at temperatures above 25 °C.

Effects of temperature on fish larvae of Australian commercial species were also investigated. A 30 minute LT-50 level (whereby 50% mortality of lake fish larvae is observed after 30 minutes exposure) as 35.1°C ±0.9 °C and 37 °C ±0.9 °C for anchovy and leatherjacket eggs/pro-larvae, respectively (Powles, 1974). Only the larvae of non-commercially significant species were entrained into the cooling water intake (Powles, 1974). Generally, species that are of commercial interest are species that breed in the ocean and enter the estuary as post-larvae and juveniles and migrate to seagrass beds and mangrove areas (ECNSW, 1983).

1.5.4.4 Phytoplankton

The most recent study (2000-04) of phytoplankton in Lake Macquarie formed part of a broad-scale sampling program examining spatial and temporal variability within the Tuggerah Lakes estuary, Brisbane Waters and southern Lake Macquarie. The study excluded thermal plume affected sites. However, the study identified that species richness of each of the lakes was similar (Roberts and Barnes, 2004). Differences in assemblages between lakes were predominantly caused by a subset of taxa, mainly of unidentified flagellates and *Chaetoceros* spp.

For the Vales Point discharge, a reduction in the standing crop size and mean annual chlorophyll-a concentrations at sites adjacent to the outfall has been reported (AWACS, 1995). Generally, phytoplankton studies for the lake have focused on issues associated with algal blooms as lake-wide issue. Some studies indicated that phytoplankton blooms occurred regardless of season but followed significant freshwater inflow and rain events (MacIntyre, 1993). Others indicated that blooms of *Noctiluca scintillans* within the northern part of the lake (1955-1985) increased during periods of low rainfall and nutrient loading associated with sewage discharges (AWACS, 1995). Longer-term studies of chlorophyll-a concentrations identified a peak in lake chl-a concentrations in the early 1990's (Eyre, 2005) coinciding with a peak in lake nutrient concentrations (AWACS, 1995).

1.5.4.5 Water quality and nutrients

Measurements of temperature, salinity, pH, dissolved oxygen and nutrients for Lake Macquarie were first obtained by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) from June 1953 – September 1956. The dataset is the only water quality information available preceded the commissioning of Wangi Power Station in 1956. Sampling was limited for the period 1969-1973 occurring intermittently at a small number of sites by the Maritime Services Board (MSB) and the State Pollution Control Commission (SPCC).

Not until 1972 and almost a decade after the construction and operation of Vales Point (1963) did regular monitoring commence (ECNSW, 1983). Intake and discharge canal water temperatures were first recorded in 1970 and 1973, respectively (ECNSW, 1983). Water quality data collected by various agencies and power station operators have been summarised in various reports (NSWEC 1983; SPCC, 1983, AWACS, 1995). Water quality data covering the most recent period (1997-2011) was collected by the power station's operators Delta Energy and Eraring Energy under license (Eyre, 2005; Eraring Energy, unpub. data). Data for a small number of additional sites has been collected by Lake Macquarie City Council (Office of the Lake Macquarie Catchment Coordinator, pers. comm.) or as parts of other lake studies (Roberts and Barnes, 2004).

Generally, lake turbidity, nutrients and temperatures increased for the sixteen year period from 1975-1991 (MacIntyre and Holliday, 1993). Increases in annual mean surface and bottom lake water temperatures were also observed for the period 1983-1994 (AWACS, 1995). For salinity, relatively low surface values of ~30 for 1955-56, 1988-89 and 1989-90 were associated with significant high rainfall periods. Conversely, salinities of ~36 in 1993-94 (AWACS, 1995) corresponded with periods of below average rainfall and extended drought conditions (Eyre, 2005). Changes to mean concentrations of dissolved oxygen between 1953-56 and 1983-1994 were small relative to shorter-term changes. The greatest variability in dissolved oxygen concentrations associated with periods of significant freshwater inflows (AWACS, 1995).

Mean nutrient concentrations within the lake increased significantly from 1950s to the 1990s most likely attributed to increased urbanisation, catchment runoff and sewage inputs (SPCC, 1983; AWACS, 1995). Increases in soluble phosphorus (orthophosphate) over 1953-1983 was most significant for the relatively more urbanised northern part of the lake (SPCC, 1983). While ranges of nitrate concentrations (1-48 $\mu g\ L^{-1}$) did not appear to change between the 1950s and 1980-90s, orthophosphate increased 3-fold from a mean of 8 $\mu g\ L^{-1}$ to 14-27 $\mu g\ L^{-1}$. Annual mean chlorophyll concentrations during 1983-94 were generally $\leq$3.0 $\mu g\ L^{-1}$ peaking during 1988-1991 at ~5.5 $\mu g\ L^{-1}$ (AWACS, 1995). Since the redirection of sewage to the ocean, concentrations of nutrients within the lake dramatically declined (Eyre, 2005). Under current conditions, lake nutrient concentrations are driven by more diffuse sources such as urban runoff and nutrient loads delivered by intermittent stormwater flows (AWACS, 1995).

1.5.4.6 Heavy Metals

Heavy metals within sediments and biota of Lake Macquarie and derived from industry on the lakes shores and within its catchment have been reported widely (Crawford et al., 1976; Roy and Crawford, 1984; Batley, 1987; Peters et al., 1999a; Peters et al., 1999b; Roach et al., 2008; Olmos and Birch, 2010). While lead (Pb), cadmium (Cd), zinc (Zn) and copper (Cu) are the main metals of concern, selenium (Se) has also been studied widely due to its association with fly ash and power station operations. Concentrations of metals in surficial sediments generally decrease from north to south with maximum concentrations adjacent to Cockle Creek. Cockle Creek received effluent from a number of industries including a Pb-Zn smelter in operation for the period 1897-2003 (AWACS, 1995). During operational times, smelting resulted in the discharge of up to ~50 $ML day^{-1}$ (Furner 1979 in Batley, 1987) of effluent to the lake with elevated concentrations of lead, zinc, cadmium and copper (Roy and Crawford, 1984; Batley 1987). Cores obtained in lake sediment surveys indicated that metal concentrations at sites adjacent to smelter reach subsurface (100-450 mm) maxima of 6000 mg kg^{-1}, 600 mg kg^{-1}, 6250 mg kg^{-1} and 305 mg kg^{-1} for Pb, Cd, Zn and Cu, respectively. Exposure of the wider lake environment to elevated concentrations of metals is demonstrated by the presence of a similar zone of contamination in sediments cores from elsewhere in the lake (depths of ~150-350 mm in Roy and Crawford, 1984).

Evidence for the bio-transference of elevated metal species in Lake Macquarie sediments to benthic fauna has been demonstrated for Se but not for Cu, Zn, Cd, As and Pb (Barwick and Maher, 2003). Selenium associated with fly ash, a bi-product in the burning of coal, enters the lake from stack emissions or via runoff from power station ash dams and becomes incorporated into bottom sediments (Davies and Linkson, 1991; Peters et al., 1999a) and has constituted up to 20-40% wet weight of sediment in the past (Crawford, 1976). From studies of metals in sediments, however, selenium concentrations were close to background levels or at detection limits for southern lake sites distant from power stations. Concentrations generally ranged around 0.2-0.5 μg g^{-1} for Crangan Bay, ~ 5.6 μg g^{-1} Chain Valley Bay and 1.8-5.8 μg g^{-1} Wyee Bay. Downstream of the ash dam in Mannering Bay concentrations reached ~ 8.8 μg g^{-1} (Peters et al., 1999a; Roach 2005) compared to ~ 21-22 μg g^{-1} within Vales Point Power Station fly ash (Davies and Linkson, 1991).

A sediment core from a site adjacent to the power station in Mannering Bay indicated selenium concentrations were enriched toward the surface (10.5 μg g^{-1}) and decreasing with depth to <3 μg g^{-1} at 200 mm (Peters et al., 1999a). The combination of metal profiles and ^{210}Pb dating confirm that the greatest contamination of sediments with Se occurred post-1960s (Peters et al., 1999b) coinciding with the commissioning of Vales Point power station. While low level enrichment was apparent much deeper in the core to ~1864 ± 20 years, remobilisation of Se within pore waters of core sediments may be responsible for an apparently earlier pre-contamination boundary (Peters et al., 1999b).

A series of other metals found within NSW bituminous coals including vanadium, zinc, copper, boron and germanium (Swaine, 1985) have also previously been found to be present at elevated concentrations in lake sediments (Batley, 1987). More recent changes to ash dam management practices (1996), however, are expected to have reduced metal contamination to Wyee Bay (Peters et al., 1999b). The most recent studies of Lake Macquarie sediments indicate that the greatest contamination remains in the north adjacent to Cockle Creek and hotspots adjacent to the two operating power stations (Olmos and Birch, 2010). Surface sediments throughout the lake remain enriched relative to background even though, generally, concentrations have declined since the 1970-80s (Roach, 2005).

1.5.4.7 Selenium

Se enters the lake as selenite, selenate or elemental selenium and becomes incorporated into bottom sediments. Generally, Se becomes immobile in sediments under anoxic conditions (Peters et al., 1999b). In aerobic sediments, however, Se become relatively mobile and forms selenite, selenate and biselenite compounds (Masscheleyne, et al., 1991) with selenite the preferred compound for uptake by phytoplankton (Price et al., 1987). Selenium enters the base of the food web complexed within phytoplankton and bacteria as selenocysteine and selenomethioine (Bottino et al., 1984 in Peters et al., 1999a). Although selenium is an essential element, elevated concentrations can have implications for food chains and organism physiology and biomagnification is the major route for the concentration of selenium for marine animals (Zhang et al., 1990).

Peters et al. (1999a) identified concentration of Se in polychaete and mollusc tissue at 11 and 5 times greater in Mannering Bay compared to those from Nord's Wharf (Crangan Bay), respectively. A positive correlation between concentrations of selenium in sediments and fish muscle tissue for 5 benthic-feeding species in the lake was also established (Peters et al., 1999a). Concentrations of Se, Pb, Cd, Cu and/or Zn in muscle and gonad tissue of several fish species in Lake Macquarie were greater compared to that for other pristine NSW estuaries (Kirby et al., 2001; Roach et al., 2007).

In particular, selenium in the lake has reached levels considered to significantly effect growth, reproduction and survival of sea mullet (Kirby et al., 2001). Selenium also features as a contaminant of significance in the sediments and biota of freshwater cooling ponds associated with coal fired power stations in inland areas of NSW. A study of selenium in water, sediments, infauna and fish from Lake Wallace, a cooling reservoir for Wallerawang Power Station, in south-western NSW demonstrated biomagnification and larval stage teratogenesis for some fish species but not others (Jasonsmith et al., 2008). Generally, concentrations of metals in sediment, fish and infauna of Lake Macquarie indicate that the whole lake has been contaminated relative to background and that selenium has contributed to the lakes food web (Batley, 1987; Peters et al., 1999a).

2. Thermal Plume Effects

A multi-disciplinary approach for assessing effects of thermal

pollution on estuaries using benthic diatoms

and satellite imagery.

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Chapter 2 - Thermal Plume Effects: A multi-disciplinary approach for assessing 55 effects of thermal pollution on estuaries using benthic diatoms and satellite imagery. pp 55-84

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3. Community Shift

Palaeoecological evidence for change in an estuarine embayment

receiving thermal discharge from a power station,

Lake Macquarie, New South Wales,

Australia.

Abstract

In the absence of adequate baseline data for the management of the effects of thermal effluent plumes on coastal ecosystems, palaeoecological reconstructions are powerful techniques that can be used to infer past condition. Fossil diatom assemblages preserved within sediments of a bay exposed to a thermal plume for a decade prior to monitoring in Lake Macquarie, Australia, were used to reconstruct a water quality history. The work forms part of a larger investigation to determine the potential of using benthic diatoms as a biomonitoring tool for thermal discharge effects on coastal lakes in New South Wales. Assemblages within the core exhibited periods of relative homogeneity and heterogeneity and an overall temporal shift in species assemblages from 1910 to 2003. *Navicula robertsiana* dominated assemblages during the pre-power station period (1910-1963) and *Trachyneis aspera* represented the phase following commissioning (1963-1989). *Navicula rhaphoneis*, *Tryblionella lanceola*, *Tryblionella punctata* var. *coronata*, *Paralia* sp., *Surirella globosa* and *Stephanopyxis turris* dominated assemblages for the most recent period of reduced power station output (1989-2003). Salinity, temperature and phosphate were the most significant (p<0.02) and independent variables explaining species variability in the reference dataset. These parameters were then used to develop transfer functions using both linear and unimodal methods. Linear partial least squares models performed best and were used to reconstruct salinity (r^2= 0.95, r^2boot= 0.85, RMSE= 1.05, RMSEP= 1.10) and temperature (r^2= 0.83, r^2boot= 0.59, RMSE= 1.12 °C, RMSEP= 1.20 ºC) since 1910. Reconstructed temperature indicated a greater variability in temperature with the onset of power station operations. Although reconstruction error values for temperature were ± 1.1 °C a long-term changes in water temperature for the 20th century was comparable to that for regional air temperature. Shorter term inter-slice temperature variability was not quantifiable. This study demonstrates the value of multivariate approaches and benthic diatoms as powerful tools for delineating changes in estuarine ecology and identifying water quality baselines.

3.1 Introduction

With a range of anthropogenic pressures placed on coastal ecosystems as a result of population growth as well as urban and industrial, sustainable management of estuaries must now also consider implications associated with a change in climate. Resilience of environments to climate impacts is likely to be improved by a reduction of non-climate stressors (Department of Climate Change and Energy Efficiency, 2009). Thus, monitoring and environmental assessments must be able to delineate the effects of climate from those induced by pressures such as pollution. Bioindicator-type community assemblage and multiple taxa approaches are one quantitative method that is increasingly being applied to improve understanding of ecosystem structure and function, and detect effects of multiple stressors on ecosystem health (Niemi et al., 2004).

The implications for systems responding to changes in temperature are of particular concern with respect to changing climate conditions. The significance of temperature to the functioning of systems and distribution of species, including phytoplankton are reported widely (review in Finkel et al., 2010). Phytoplankton respond to thermal gradients over various spatial and temporal scales in natural systems. For example, distributions of diatoms relative to sea surface temperature in oceanic systems (Zielinski and Gersonde, 1997; Crosta et al., 2005; Esper et al., 2010), regional-scale (Pienitz et al., 1995; Weckström et al., 1997) and temporal (10,000 years) climatic gradients (Cremer et al., 2001) have been reported. Climate-associated temperature changes in coastal systems have facilitated range extension of planktonic or plankton-associated species in open coastal systems (e.g. *Noctiluca scintillans* in Hallegraeff et al., 2008; *Centrostephanus rodgersii* in Banks et al., 2010).

In closed systems, the significance of temperature as a driver of the distribution of diatoms has been described in relation to discharges from thermal springs to rivers (Boylen and Brock, 1973; Vinson and Rushforth, 1989) or across broad geographical areas (Weckström et al., 1997). For estuaries, distributions of benthic diatoms have been described in association with an artificial temperature gradient and a power station discharge plume (Chapter 2 – Ingleton and McMinn, 2012). Most commonly for estuaries, however, diatom distributions have predominantly been associated with natural (Saunders, 2010) and artificial gradients of nutrients and salinity (Underwood et al., 1998; DelaCruz et al., 2006).

The ecological implications for artificially induced temperature change in response to thermal discharges are varied. Contemporaneous multi-taxa assessments of the effects of thermal discharges have utilised fish (Sandström, 1991; Teixeria et al., 2009), plankton (Keskitalo, 1987; Chuang et al., 2009), macrophytes (Squires et al., 1978), benthic fauna (Lardicci et al., 1999; Bamber and Spencer 1984) and diatoms (Snoeijs, 1991). Thermal discharges can eliminate local and encourage invasive fish species (Thomas et al., 1986). For the phytoplankton, changes to temperature regimes can affect physio-chemical processes and food web interactions (Finkel et al., 2010), alter patterns of dominance in (Anraku, 1974) and reduce species diversity (Hein and Koppen, 1979) and abundance (Rajadurai et al., 2005). Investigations involving benthic diatoms, in particular, are advantageous as bioindicators because they are more abundant than other benthic and aquatic organisms, and lend themselves to both contemporaneous and palaeoecological investigations (Moser et al., 1996).

Successful management of environmental systems requires the determination of pre-impact and current conditions, ranges of natural variability and an understanding of the extent and direction of change (Weckström et al., 2004). In Australia, population growth and development has been focused along the coast (Roy et al., 2001) and as a result many estuaries have been moderately to extensively modified (National Land and Water Resource Audit, 2002). In many cases, information on the pre-condition of systems prior to anthropogenic disturbance is limited or completely absent (Saunders et al., 2008). In these cases palaeoecology is a powerful tool whereby biological data preserved within the sediments can be retrieved and utilised to reconstruct a water quality history (Saunders and Taffs, 2009). Such techniques can be used to determine the direction and nature of anthropogenic induced change in the absence of adequate baseline data (Weckström et al., 2004) and are considered among the most powerful techniques for identifying suitable reference conditions within aquatic systems (Dixit et al., 1992).

In Australia, palaeolimnological techniques for reconstruction of water quality and/or climatic trends have been used for wetland systems (Tibby and Tiller, 2007), coastal marshes and estuarine-brackish environments (Reid, 1997; Taffs et al., 2008: Saunders et al., 2008; Logan et al., 2011). Temperature is considered to be a less of a driver of diatom variability when other variables (salinity, pH, phosphate) dominate (Bilger and Hall, 2003). Diatom-inferred functions, however, may be considered appropriate proxies for temperature over historical time scales or where extremes in temperature have been induced associated with anthropogenic pressures (Anderson, 2000). An estuary receiving a power station thermal discharge would be an example of a modern environment exposed to such temperature extremes. Previous studies utilising a palaeoecological technique to reconstruct a diatom-inferred temperature history for an estuarine bay affected by a thermal discharge have not been reported.

Three coal-fired power stations currently operate on the New South Wales (NSW) central coast, Australia (Figure 3.1). The stations draw water from adjacent coastal lakes to cool generator turbines, and then discharge water up to 12 °C above ambient temperature back into these systems (SPCC, 1983). The work described here forms part of a larger investigation to determine the potential of using benthic diatoms as a biomonitoring tool for thermal discharges to coastal lakes in NSW. Initial work (Chapter 2 – Ingleton and McMinn, 2012) identified changes in the relative abundances of key contemporaneous benthic diatom species in response to the thermal plume from Vales Point power station.

The aim of this study was to examine the changes in fossil diatom assemblages over time at a site affected by thermal pollution from a power station cooling water discharge. The study tested the null hypothesis that there is no significant difference between the pre- and post-power station assemblages in Wyee Bay. A palaeoecological approach was used to develop models and reconstruct histories for the strongest and most independent variables driving gradients within the dataset. Reconstructions were then tested against long-term monitoring data and baseline conditions for environmental variables were inferred.

3.2 Background

3.2.1 Location and Geomorphology

Lake Macquarie is situated on the temperate south-east coast of Australia at 33.1 °S 151.5 °E (Figure 3.1a). The lake is relatively large (20 km x 10 km) and deep (mean 4.6 m, max. 11 m), and formed 12-6 ka years ago towards the end of the last marine interglacial transgression (Thom and Chapel, 1975). The lake is classified as a wave-dominated back-barrier coastal lake forming as an impoundment of water at the junction of several river valleys behind a barrier of marine sand (Roy et al., 1980).

The lake is a low energy mud basin that receives a limited sediment load via relatively small creeks and catchments (Roy and Peat, 1975). Tidal currents are limited to the entrance channel with tidal exchange at <1% of lake volume per cycle. Circulation in the upper embayments is driven by locally generated wind waves (<1m) (Spencer, 1959; AWACS, 1995) and most of the lake bed is below effective wave base, which limits sediment re-suspension (Roy and Crawford, 1984). Lake depth and restricted tidal exchange function so that after periods of heavy rainfall, sediment is generally retained within the lake basin and not lost to the ocean.

Unconsolidated Holocene sediments are predominantly estuarine mud extending to 21.5 m below sea level, up to 12 m thick at the base and dated to ~7500 years ago (Roy et al., 1980). Work by Batley (1984) on sediment core lead and zinc profiles from within the lake calculated sedimentation rates of between 1.1-5.7 mm year^{-1}. Sediments of the lake contain a relatively continuous record of mid to late Holocene deposition (Roy and Crawford, 1984) and like other estuaries in the region their evolution has facilitated the preservation of an invaluable sedimentary and palaeoecological record (Nichol, 2001). While the lake's catchment is considered only moderately developed (OzCoasts, 2009), the estuary itself has been impacted by significant industrial and urban development. While nutrient levels have declined with the redirection of sewage (AWACS, 1995), contamination of the lake with heavy metals (Roach, 2005; Olmos and Birch, 2010) is a legacy that continues to effect lake ecology (Peters et al., 1999; Roach et al., 2008).

3.2.3 Power Station Operations

Construction of power stations on the NSW central coast commenced in the 1950s due to the proximity of coal reserves (e.g. 12 Bt Hunter Valley, NSW Department of Primary Industries 2006-07) and access to water bodies that could be utilised as sources and sinks for turbine cooling water. Vales Point Power Station lies on the shores of south-western Lake Macquarie (Figure 3.1b) and was commissioned in 1963 with a capacity of 600 MW. Capacity increased with commissioning of additional turbines, reaching 875 MW in 1966 and 2195 MW in 1978. Replacement of the original turbines in 1989 resulted in a reduction of capacity to 1320 MW to present.

The station uses lake water drawn in from Chain Valley Bay to cool its turbines and then discharges the water back into the lake at the southern end of Wyee Bay with a licensed discharge maximum temperature of 35 °C and limited release maximum of 37.5 °C (NSW Office of Environment and Heritage (OEH) Environment Protection Licence 761). Monitoring of the discharge plume and lake receiving waters commenced in 1973 (SPCC, 1983).

Wave dominated barrier estuaries, by their shallow and tidally restricted nature, are susceptible to unnatural changes in temperature (Heap et al., 2001). Early studies concentrating on benthic effects of the heated water plume from Vales Point Power station concluded that the impact on benthic organisms was localised and regionally insignificant (ECNSW, 1983; SPCC, 1983; LMCC, 1997). Changes to the distribution of seagrasses, however, have been attributed to thermal pollution from power stations in the lake (ECNSW, 1983), as well as decreased abundance of shallow water (<1m) invertebrates (Robinson, 1987) and mussels (Wallis, 1976).

More recent investigations using epibenthic diatoms indicated significant changes in species relative abundance with distance to within 2000 m of the discharge point and to at least 4.7 m water depth relative to adjacent embayments (Chapter 2 – Ingleton and McMinn, 2012). While stratification was a dominant feature of the water column to within ~1500 m of the outfall, vertical stratification was limited to <1 °C further downstream where water depths increased and Wyee Bay opens to the

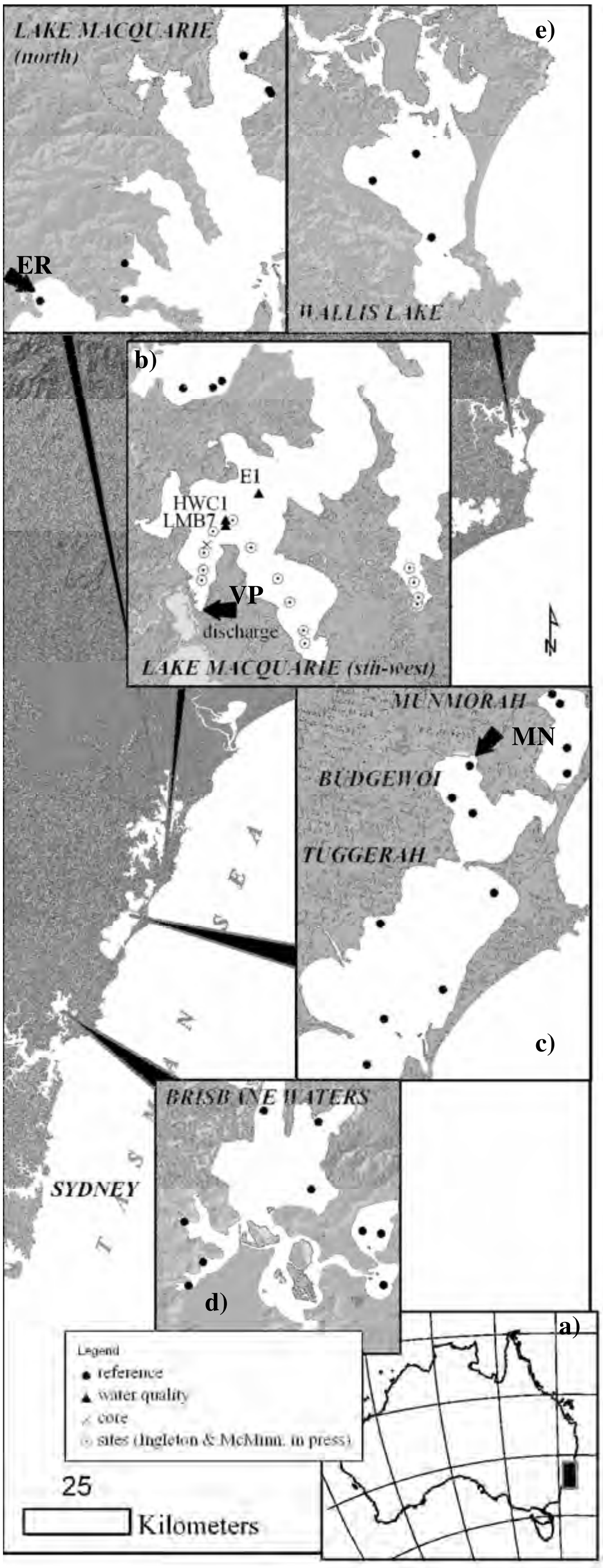


Figure 3.1 Location of sampling sites in southern Lake Macquarie, New South Wales, Australia. Arrows denote location of power station thermal discharges for Eraring (ER), Vales Point (VP) and Munmorah (MN).

lake's south-western broadwater. Plume temperature gradients and extents were seasonally variable. Sediments were exposed to temperatures elevated above ambient of >0.5 °C (ΔT) as far as the adjacent intake bay at times (Chapter 2 – Ingleton and McMinn, 2012). Control locations routinely utilised elsewhere in the lake are affected by other diffuse pollution pressures (e.g. heavy metals in Roach, 2005) and thus, benthic assemblages at these sites are not likely truly representative of non-anthropogenic conditions.

3.3 Methods

3.3.1 Reference Dataset

To develop a reference dataset, environmental data and benthic diatoms were obtained from sites across the NSW central coast lake systems during the period March 2008 to July 2009. Temperature, salinity, turbidity, dissolved oxygen and pH data were collected at each sampling location using a Yeo-Kal 612 Water Quality Analyser (YeoKal Electronics, Australia) at the surface (0.2 m), 0.5 m, 1 m and at 1 m intervals to the lake bottom. Water samples collected within 0.5 m of the surface were filtered through 0.45 µm filters into 30 mL vials and frozen at -4 °C prior to dissolved phase nutrient analyses of ammonia, oxidised nitrogen, orthophosphate and silica. Nutrients were analysed using a Lachat QuikChem 8000 (Hach Company, USA) flow injection analyser (FIA) with quantification limits of 5 µg L^{-1} for silica and 1 µg L^{-1} for the other nutrients analysed. A summary of water quality parameters presented as lake medians are presented in Table 3.1.

Diatoms within surficial sediments were obtained using a modified passive gravity corer. Sediments were extruded onsite and the top 0.5 cm of wet sediment was retained for diatom analysis. A similar methodology for developing diatom reference datasets has been utilised by previous studies (e.g., Weckström et al., 1997; Tibby et al., 2007; Saunders et al., 2008). Single sediment samples were obtained from 31 sites across Lake Macquarie, the Tuggerah Lakes including Tuggerah, Munmorah and Budgewoi broadwaters (Figure 3.1c) and the Brisbane Waters estuary (Figure 3.1d). To provide a comparison to a less affected estuarine lake system from outside the Sydney basin (classification in Ozcoasts, 2009); an additional three sites in

Wallis Lake were sampled in October 2007 and included in the analysis (Figure 3.1e). Mean relative abundance (RA) species scores and water quality data from triplicate sample sites (15 sites) in the three southern bays of Lake Macquarie, Wyee Bay, Chain Valley Bay and Crangan Bay (Chapter 2: October 2002 - February 2003), were also included. In total, 49 sites were available for use in the reference dataset.

3.3.2 Paleo-Historical Dataset

A single core approximately 23 cm in length was obtained from within Wyee Bay (WB1C) at 33º 8.6’ E and 151º 31.9’ S on the 10 October 2002 at a water depth of 4.8 m (Figure 3.1b). The site was located within the central basin of the receiving water embayment, free of seagrasses and less affected by wind wave action compared to shallower (<2–2.5 m) sites. From temperature data obtained in Chapter 2 bottom water temperatures at the site experienced ΔT of between 0.5-1.0 °C (maximum ~ 3 °C, see Chapter 2 – Ingleton and McMinn, 2012). The top 10 cm of the core was extruded on site by sub-sampling at 0.5 cm intervals and 5-10 g wet weight sediment from each subsection was transferred to sterile 50 mL centrifuge tubes. The remainder of the core was capped and transported back to the laboratory and later sub-sectioned at 1 cm intervals (from 10-23 cm). All sediment samples were stored in the dark at 2-4 ºC prior to analyses.

Monthly water quality monitoring data for Lake Macquarie was obtained from various reports and datasets including the Commonwealth Scientific and Industrial Research Organisation (CSIRO) (1953-1955), State Pollution Control Commission (SPCC) (1983), Electricity Commission (EC) NSW (1983), Hunter Water Corporation (HWC) (1999), Eyre (2005) and unpublished data from Eraring Energy (2002-2003). Data for the other lakes were contained within the NSW OEH Coastal Eutrophication Risk Assessment Tool (CERAT) (2010) and NSW OEH (2011). Monthly salinity, temperature and phosphate data were used to calculate time-depth averaged medians (core slice median - CSm) for the time period represented by each core slice as determined from ^{210}Pb dating. CSm values were calculated for Wyee Bay (using monitoring sites in Figure 3.1b - E1: 1973-1982, Site HWC1: 1983-1997, LMB7: 2002-2003), the lake body (various lake-wide sites - n=15: 1953-1956, n=4: 1973-1983; n=13: 1983-1997; n=3 2002-2003) and deltaT (ΔT – the difference between Wyee Bay monitoring site temperature and lake median temperature) for comparison to diatom-inferred model values for the period 1953-2003. Site E1 was located ~2000 m, HWC1 ~500 m and LMB7 ~450 m further from the discharge point than the WB1C core site location. Thus, all sites were likely to underestimate ΔT in comparison to what is represented at the core location with the 1973-1982 (site E1) data period likely to exhibit the greatest temperature offset. An estimated difference in median surface water temperature between sites E1 and HWC1 was in the order of <1 °C according to previous water quality surveys (Chapter 2 – Ingleton and McMinn, 2012). Power station output, Wyee Bay lake water monitoring sites (LM14 and LMB7 in Eyre, 2005), inlet or outlet canal temperature data were not available.

Total monthly rainfall (Wyee station 61082), monthly mean daily maximum air temperature (MMDMAT Nobbys Head, Newcastle station 61055) and mean monthly El Niño Southern Oscillation Index (SOI) data for the period 1910-2003 were obtained from the Australian Bureau of Meteorology (BOM) climate data online website (BOM, 2010). Monthly air temperature anomaly values were calculated by subtracting each MMDMAT value from a calculated 1910-2003 monthly median. CSm for air temperature anomaly, SOI and rainfall were then calculated for comparison with historical water quality CSm values. Anomalies are values determined for each individual point in a time series calculated by subtracting the variable from the mean value for that variable across the entire series (Makridakis et al., 1998). The values provide an indication of when conditions are "anomalous" compared to average conditions.

3.3.3 Sediment sample processing

Approximately, 1-2 g of wet sample from each core slice was weighed into 50 mL vials and treated with a cold digestion of 20-25 mL of 10% hydrogen peroxide (H_2O_2) for 48-72 hours to remove organic matter. The overlying supernatant was then siphoned off settled samples before 20-25ml high purity water (0.2 µm filter), a broken coverslip and 5-10 drops of 5% glacial acetic acid were added to each vial.

The contents of each vial was gently mixed before pipetting 1-3 mL suspended sediment onto cleaned 40x22 mm coverslips and left to dry in a dust free environment. Coverslips were then permanently mounted on pre-labelled glass slides using Norland Optical Adhesive 61 (Norland Products Inc., USA) and cured with ambient ultra-violet light (2-4 days). Samples were examined under oil immersion at 1000x magnification using a Leica DM 2500 compound microscope with differential interference contrast (lens 100/1.25 oil) illumination. A total of 400 or more individual diatom frustules were identified in longitudinal traverses for each slide with diatoms identified to species level, where possible, according to recent scientific taxonomic literature. Taxonomy was based on Australian references (John, 1983; Saunders et al., 2010) with reference to cosmopolitan floras in Witkowski et al. (2000). Many valves were fragmented and thus only valves where greater than half the individual specimen was intact were counted in order not to count the same specimen twice.

Bulk sediment samples were analysed for ^{210}Pb activity using alpha spectrometry as described in McMinn et al. (1997) and modified by Harrison et al. (2003). Unsupported ^{210}Pb activity data for the sediment profile were used to develop dating models using both the Constant Initial Concentration (CIC) (Robbins, 1978) and Constant Rate of Supply (CRS) techniques (Appleby and Oldfield, 1978).

3.3.4 Statistical Analyses

Prior to statistical analyses each of the environmental variables were checked for skewness (standard deviation >7). Of the 10 variables measured, salinity, dissolved oxygen, ammonia and silica were log transformed. Principle Components Analysis (PCA) was then performed to determine the major environmental gradients within the dataset.

Analysis of the species dataset was conducted using Bray-Curtis nested two-way similarity-dissimilarity analysis (SIMPER) in PRIMER 6 (Plymouth Marine Laboratories, U.K.) and multivariate techniques contained in the software package CANOCO 4.5 (Ter Braak and Šmilauer, 2002). A total of ~380 taxa were identified in the core and reference sediment samples. To reduce the effect of artificial weighting caused by the presence of a large number of rare taxa, species with an abundance of <1% in at least 1 sample or a summed relative abundance of <5% across the combined dataset were eliminated. This resulted in a total of 141 taxa retained for statistical analysis.

Gradients in the core and reference datasets were examined, separately and combined, using Detrended Correspondence Analysis (DCA) with detrending by segments and downweighting of rare species on the untransformed species data. Data was then log *(x+1)* transformed, centred and standardised, and further analysed using linear and/or unimodal methods in species and/or environment data. Monte Carlo permutation tests (999 permutations on the full model) restricted with and without split-plot structuring, with and without auto-forward selection (partial ordination) were conducted to determine the significance of environmental variables in explaining the species variability.

Transfer functions were developed in C2 version 1.6.8 (Juggins, 2010) using both Partial Least-Squares (PLS), simple Weighted Averaging (WA) with inverse and classical deshrinking and with/without tolerance downweighting, and Weighted-averaging Partial Least Squares (WAPLS) on the reference species and environment datasets. PLS and WAPLS outputs were both used to determine which models resulted in the best performing transfer functions with cross-validation by bootstrapping (n=100). Those variables that possessed the best real correlation (r^2) and predicted (r^2_{boot}) correlation, the lowest root mean square error (RMSE) and root mean square error of prediction (RMSEP), and were considered significant according to a t-test (p<0.05), were identified. The amount of independent variability explained by each of these variables within the dataset was determined by individual CCAs and the amount for 2-variables (covariables) combined using CCAs and manual forward selection. Detrended Canonical Correspondence Analyses (DCCA) were used to determine those variables where the ratio of the first axis (constrained) to the second (1st unconstrained) axis was >0.5 (Kingston et al., 1992), indicating them to be the most suitable for transfer function development (Birks, 1998). These variables were then used for diatom-inferred reconstructions. Species diversity indices were calculated for each sample using PAST 1.93 freeware package (Hammer et al., 2001).

3.4 Results

3.4.1 Reference Dataset

3.4.1.1 Environmental Data

Surface water temperature at the time of sampling ranged from 12.1-27.8 ºC compared to a long-term monitoring ranges of 11.8-30.1 °C (Table 3.1). Temperatures generally reflected the season in which sediments were sampled except for sites BW1 (~+3 ºC) and ER1 (~+8 ºC) that were adjacent to discharges from Munmorah and Eraring power stations, respectively (Figure 3.1). Median salinities indicated that at the time of sampling lakes were either predominantly saline (32.7 – 37.1) or brackish (15.9 – 26.7). Generally, the Tuggerah Lakes system exhibited consistently lower and more variable salinities over longer time scales. Values for pH were higher at the time of sampling (9.2 pH units) relative to the longer term range in Brisbane Water and Tuggerah Lake and were likely associated with periods of freshwater inflow. Similarly, higher turbidity and lower dissolved oxygen values occurred at these times.

Median ammonia surface water concentrations at the time of sampling were generally similar to or lower than long-term medians across all systems (Table 3.1). Ammonia was lowest for Crangan Bay (0.7 $\mu g\ L^{-1}$) with highest sampled concentrations for west Lake Macquarie (15.6 $\mu g\ L^{-1}$), Lake Munmorah (24.1 $\mu g\ L^{-1}$) and adjacent to a power station outlet in Budgewoi (33.8 $\mu g\ L^{-1}$). Phosphate reached a maximum value of 9.0 $\mu g\ L^{-1}$ for sites in Lake Macquarie west with lake-wide concentrations generally greater than other lakes sampled. Oxidised nitrogen across all sites was <2.1 $\mu g\ L^{-1}$ sites and generally lower than longer-term monthly medians of 4.3 - 8.1 $\mu g\ L^{-1}$. Median silica concentrations were greatest in the Munmorah-Budgewoi-Tuggerah Lakes system (709-1014 $\mu g\ L^{-1}$) compared to all other lakes (131-561 $\mu g\ L^{-1}$). Means, medians and ranges for the top six auto-forward selected (see Section 3.4.4) environmental variables are presented in Table 3.1b.

A PCA of environmental data (Figure 3.2) indicated that ~51 % of the variability was explained by the first two principle axes. Variation along the first axis was explained by phosphate while pH and dissolved oxygen explained variation for the second axis.

3.4.1.2 Epibenthic Diatoms

From the reference dataset it is apparent that while some of the dominant species are common to all sampled lakes of the region (32° 10' S - 33° 31' S), others are restricted to individual systems, sub-systems or embayments (Figure 3.3). While *Grammatophora* spp. and *Melosira sulcata* (Ehrenberg) Cleve were dominant at Wallis Lake and Lake Macquarie sites, Lake Macquarie assemblages were also dominated by *Paralia* sp. and *Surirella fastuosa* (Ehrenberg) Kützing. For the Tuggerah system of lakes the species *Stephanopyxis turris* (Greville) Ralphs, epiphytic *Cocconeis scutellum* Ehrenberg and planktonic *Cyclotella striata* (Kützing) Grunow had the highest RA for all sites (Table 3.3). Those diatoms most common to Lake Macquarie sites were not all the same species common to Brisbane Waters sites. A total of 8 additional species, uncommon in Lake Macquarie, contributed on average an additional 33 % to the total of RA scores (other category in Table 3.3) for Brisbane Waters sites. Generally, Tuggerah Lakes was least diverse with a median Shannon-Wiener diversity index of 3.1. Lake Macquarie (3.9) was generally less diverse than Brisbane Waters (4.4).

A DCA of the reference dataset indicated a gradient of 3.75 and that relationships in the dataset were unimodal. A Canonical Analysis (CA) of species only data described a separation of sites into four groups with 43 % of variability in the species and 65 % in the environmental data explained by the first two principal axes (p<0.02): 1) the Tuggerah lakes system; 2) Crangan Bay (Lake Macquarie control); 3) Lake Macquarie west, north and southwest; and 4) Wyong Water and Kincumber Bay (both part of the Brisbane Waters system) (3.6a,b). Samples from sites within Wallis Lake on the mid-north coast did not fall within any of the groupings. Salinity, temperature and depth explained the greatest proportion of variability in the environment data according to forward auto-selection with each variable significant to p<0.02.

3.4.2 Sediment, paleo and historic data

3.4.2.1 Core sediments and ^{210}Pb dating

The sediment core was comprised of homogeneous, grey-black mud (>90%, <63 µm fraction) except for a 1-1.5 cm oxic, green-brown, hydrous layer at the surface and bleached whole and fragmented bivalve shells at depths >20-21 cm. The shell layer prevented deeper penetration of the core barrel into lake sediments at this site.

Unsupported ^{210}Pb activities exhibited a linear decay profile (r^2= 0.93; n= 8) indicating that the core chronology was preserved and sediment mixing was restricted to <2 cm according to the dating inversion point (Figure 3.4). Both CIC and CRS dating models were in good agreement to a depth of 8 cm, below which point the models diverged to a maximum relative offset of ~ 17-18 years at 15-16 cm (c. 1942 cf. 1960). Although there are no large river systems discharging to Lake Macquarie, it is characteristically a mud basin and the majority of embayments are fed by creeks or rivulets. Since the CIC and CRS models are not in good agreement at depth and the CRS model accounts for possible compaction within a core and changing sedimentation rates, the CRS model was selected as the preferred dating model to be used. Sedimentation rates for the core were bimodal. An increase in the rate from 2.5 mm $year^{-1}$ at 20-21 cm to 3.7-4.1 mm $year^{-1}$ toward the surface may reflect increased catchment degradation and increased sediment loads to the lake over time (AWACS 1995; WBM Oceanics 1997). For the top 10 cm of the core, sediment slices (0.5 cm) equated to 1.2-2.6 years and 4.3-5.7 years cm^{-1} across 10-23 cm (1 cm slices).

3.4.2.2 Fossil Diatoms

Plots of the vertical distribution of the 16 most common fossil species (maximum species RA >5%) from the core are presented in Figure 3.5a. A qualitative assessment indicated that the greatest changes in species RA scores appeared to occur at 4.5-6 cm and 18-19 cm sediment depth, with a relatively smaller but discernable change in floral community composition at 12-14 cm. In the deepest sections of the core (>19 cm), the diatom flora was dominated by *Grammatophora* spp. Ehrenberg (maximum 70% RA at 19-20 cm) with 5-10% RA for *Melosira* *sulcata var. radiata* (A.I.Forti), *Melosira sulcata var. coronata* (Ehrenberg) Grunow, *Navicula lyra* var. *elliptica* (A.W.F.Schmidt) and *Trachyneis aspera* (Ehrenberg) Cleve. Sediments at 6-18 cm were dominated by both variants of *Melosira sulcata* and *Grammatophora* spp. and constituted 13-36% RA. In the top most layers (<4.5 cm), *Tryblionella lanceola* Grunow, *Navicula rhaphoneis* (Ehrenberg) Ralphs, *Paralia* sp. Heiberg, and *Stephanopyxis turris* were the most abundance species. *Navicula rhaphoneis*, which dominated surficial sediments in Wyee Bay (Chapter 2 – Ingleton and McMinn, 2012), also dominated the surface layers of the core but was almost absent from sediments older than ~1989 ± 0.9 years.

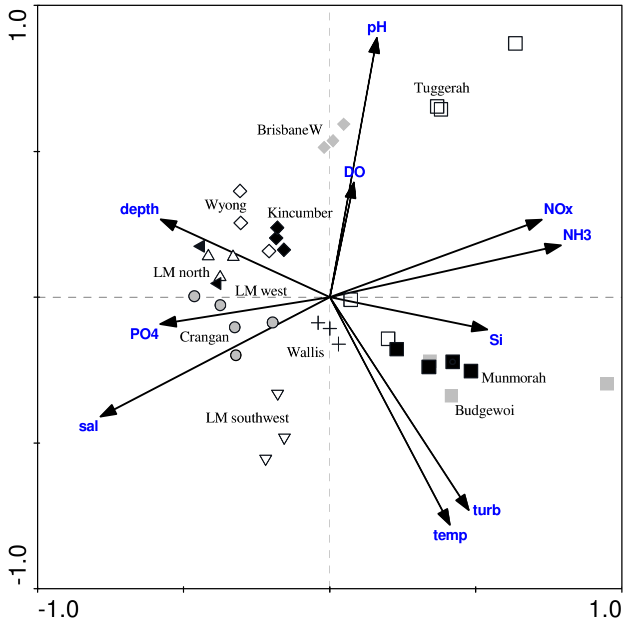
DCA on the fossil species data from the core indicated that the gradient describing variability in the dataset was 2.4. Relationships between sites within the species reference dataset were between linear and unimodal and thus further analyses were conducted using both PCA and CCA. Plots of principle components from both analyses showed a semi-circular spread of core sample depths with three discrete groupings of 5 or more adjacent depth intervals (Figure 3.6). These were defined by core depth ranges 15-19 cm (Group A) 0-4.5 cm, 6.5-14 cm (Group B) and 0-4.5 cm (Group C). A SIMPER analysis of the fossil data for these 3 groups indicated a mean within-group similarity of 77-84%. Conversely, average dissimilarity was greatest between groups A - B (62%) and A - C (70%) and least between groups B- C (25%).

Shannon-Wiener indices for core samples decreased from maximum values at the surface (0-5.5 cm) of 3.4-3.7 to a minimum of 1.2 at 20 cm (Figure 3.5b). Normalised against sediment depth (0.1 SW units cm^{-1}), changes in fossil diatom assemblages across the 1989 boundary were significant (p<0.02) with an increase in the mean diversity index from 3.39 (Group B) to 3.86 (Group C).

Table 3.1a Environmental variables for modern analogue reference sites and long-term water quality median and range from CERAT.

Estuary	Environmental variable									
	Depth (m)	Temp (°C)	Salinity	Turbidity (ntu)[3]	Dissolved oxygen (% sat)	pH	NH_3-N ($\mu g\ L^{-1}$)	PO_4-P ($\mu g\ L^{-1}$)	NO_x-N ($\mu g\ L^{-1}$)	SiO_2 ($\mu g\ L^{-1}$)
Wallis Lake[1]	3.0-3.5	20.9	32.7	6	101	8.2	5.0	0.8	0.7	434
		(20.5: 13.3-29.0)	(32.3: 18.5-36.8)	(2: 0-45)	(104: 86-156)	(9.2: 6.7-9.4)	(3.8: 0.7-20.7)	(0.5: 0-3.2)	(0.9: 0.1-19.3)	(265: 24-1811)
Lake Macquarie[2]										
North	3.2-3.3	14.9	34.0	0	101	8.2	1.9	7.4	0.3	348
		(20.3: 11.8-28.7)	(34.1: 2.1-36.8)	(4:1-24)	(98: 1-155)	(8.3: 7.5-8.8)	4.1 (0-107.1)[3]	(24.8: 6.8-155.6)	(5.9: 1.5-34.8)	-
West	2.5-5.0	15.9	34.2	0	98	8.2	2.3	7.9	0.3	341
		(20.3: 12.4-28.0)	(34.5: 8.2-37.5)	(3: 0-12)	(96: 2-114)	(8.3: 7.2-8.8)	-	(13.3: 1.5-62.3)	(5.0: 1.0-82.3)	-
South-west	3.0-3.3	26.6	37.1	7	98	8.0	1.2	5.7	0.4	548
		(21.2: 12.2-28.6)	(33.9: 7.0-37.9)	(3: 0-8)	(96:7-109)	(8.6: 7.4-8.8)	-	(12.7: 1.2-54.9)	(4.8: 0.8-46.7)	-
South	3.4-7.2	22.1	36.1	3	92	8.3	0.7	3.3	1.3	341
		(20.8: 12.7-30.1)	(34.1: 18.2-37.8)	(2: 0-27)	(98: 1-127)	(8.3: 7.5-8.8)	-	(14.0: 1.2-64.7)	(4.2: 0.2-76.4)	-
Central Coast										
Lake Munmorah	1.6-3.4	25.8	23.4	7	93	8.1	9.1	0.8	1.9	1014
		(18.8: 12.8-26.1)	(30.1: 20.8-35.1)	(4: 2-12)	-	-	(4.0: 1.6-89.1)	(0.9: 0-3.2)	(1.5: 0.4-7.0)	(521: 29-2023)
Budgewoi	1.6-2.5	27.8	23.0	11	100	8.2	6.4	0.6	1.6	907
		(19.7: 12.7-28.3)	(30.1: 4.5-35.3)	(5: 1-114)	-	-	(7.4: 1.9-67.6)	(0.7: 0-2.4)	(2.0: 0.1-18.4)	(566: 114-1265)
Tuggerah[4]	2.6-3.2	15.9	15.9	1	104	9.2	7.4	0.7	2.1	709
		(19.7: 12.6-28.3)	(30.2: 4.5-35.3)	(4: 1-114)	(101: 86-134)	(8.9: 7.6-9.5)	(4.0: 0-129.8)	(0.7: 0-24.9)	(11.2:1.0-293)	(450: 0-2402)
Brisbane Waters[5]		(20.9: 12.3-27.6)	(33.3: 0.4-36.3)	(5: 0-308)	(92: 10-123)	(8.1: 6.6-9.9)	(45.1: 13-751)	(9.9: 0.3-160)	(1.5: 0-101.7)	-
Kincumber Bay	2.5-3.2	12.1	33.2	4	98	8.5	4.2	2.9	1.3	131
Brisbane Water	4.1-4.5	17.2	26.7	0	100	9.2	6.6	1.4	1.7	561
Woy Woy Water	3.0-4.2	12.1	33.0	3.0	98.9	8.6	4.0	5.3	1.2	137

[1]long-term data source: NSWOEH 2005-2008 n=15-34, [2]data source: Hunter Water Corp. 1983-1997 n=336, [3]data source: SPCC/HWC 1974-1995 n=3801; [4]data source: NSWOEH 2005-2010 n=181, [5]data source: Gosford Shire Council 1996-1998 n=337, [4]ntu = nephelometric turbidity units as a measure of turbidity and equivalent to a 2-point (0, 100) calibration of standard Formazin solutions.



PCA	1	2	3	4
eigenvalues	0.316	0.245	0.155	0.093
Cumulative % variance of environmental data	31.6	56.1	71.6	81.0

Figure 3.2 A biplot representing scores from a PCA of environmental data for Central Coast reference sites (axes 1 and 2); and PCA analysis output of eigenvalues and cumulative % of variance explained by the first 4 axes. Symbols denote core depths (○) and other symbols denote reference sites as per Chapter 2 sites (●, ●, ●), additional Lake Macquarie sites (▲, ◀, Δ), Tuggerah Lakes sites (■, □, ■), Brisbane Waters estuary sites (◊) and Wallis Lake sites (+).

Table 3.1b Summary of environmental gradients for the Central Coast reference dataset. (first 6 auto forward-selected variables – see CCA analyses section 3.3.4).

(n=49)	Temp (°C)	Salinity	NH_3-N ($\mu g\ L^{-1}$)	PO_4-P ($\mu g\ L^{-1}$)	NO_x-N ($\mu g\ L^{-1}$)	SiO_2 ($\mu g\ L^{-1}$)
range	12.1-31.6	14.4-37.4	0.2-115.0	0.1-9.0	0.1-7.3	25-1179
mean	21.6	31.3	7.8	3.5	1.7	535
median	22.7	34.0	4.6	2.9	1.4	518

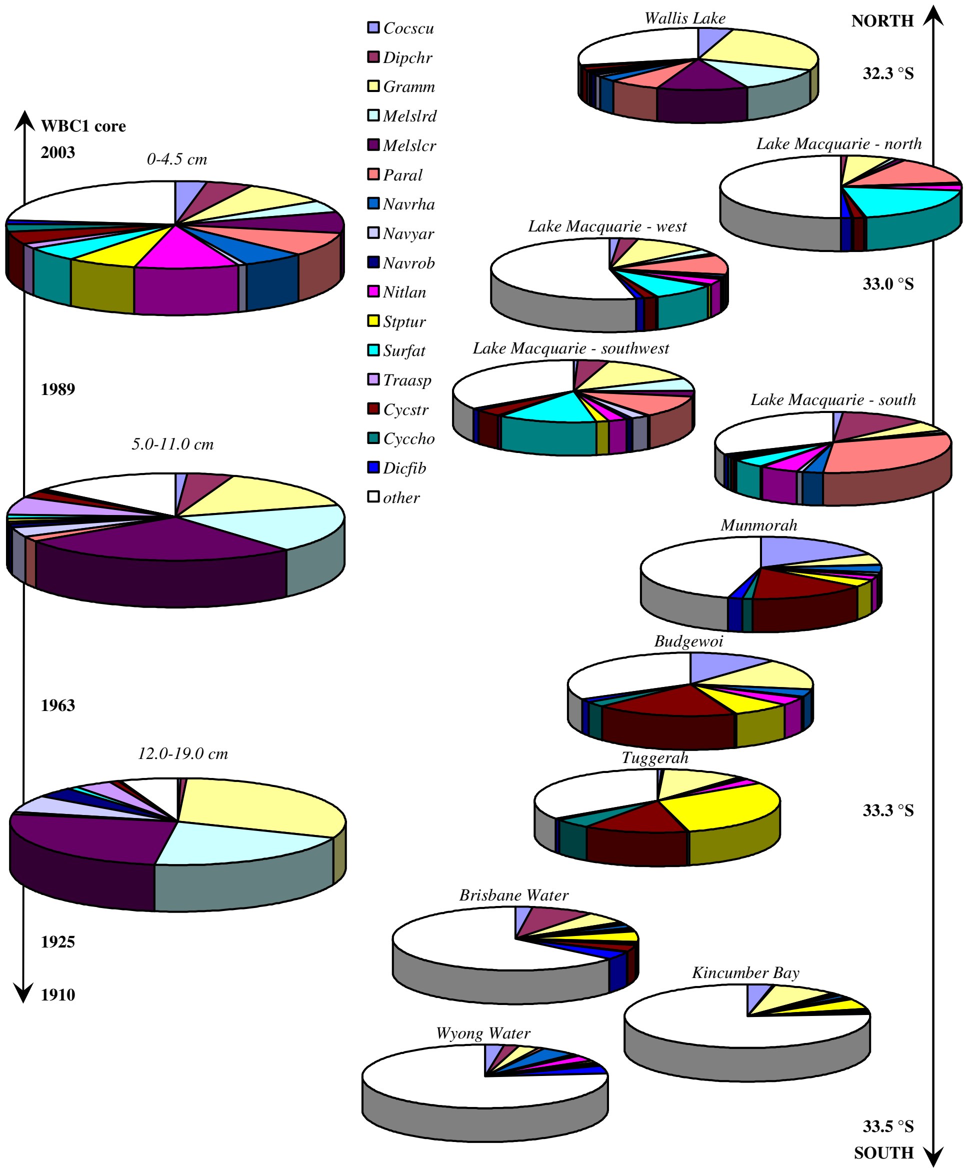


Figure 3.3 Relative abundances for 16 most common species for the receiving bay core (WB1C) and central coast training set sites. Full names for abbreviated species are presented in Table 3.2.

Depth (cm)	Total ^{210}Pb (Bq kg^{-1})		Uncorrected Unsupported ^{210}Pb (Bq kg^{-1})	
0.0-0.5	64.2	±2.6	61.0	±2.6
2.0-2.5	68.9	±2.5	66.2	±2.5
5.0-5.5	61.0	±1.8	57.8	±1.8
7.5-8.0	59.0	±2.3	55.9	±2.3
9.5-10.0	51.0	±2.1	47.9	±2.1
12.0-13.0	39.3	±1.1	37.0	±1.2
15.0-16.0	30.9	±1.0	28.4	±1.0
20.0-21.0	7.7	±0.2	5.8	±0.2

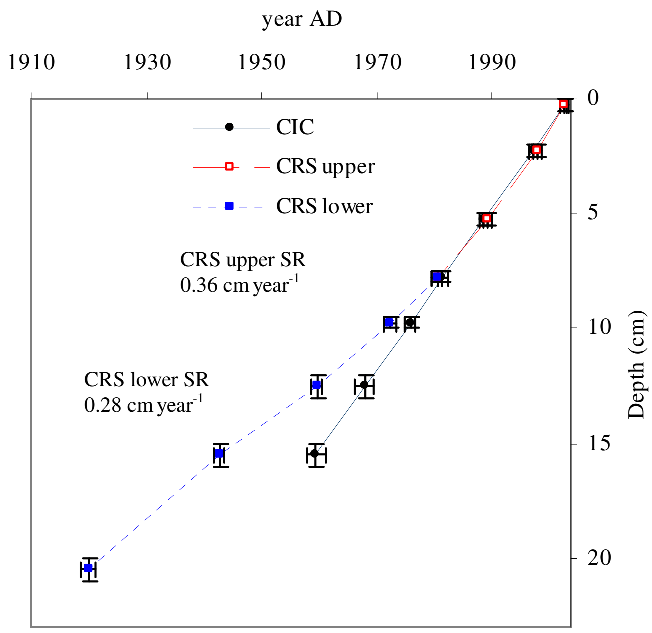


Figure 3.4 Total and unsupported ^{210}Pb concentrations with plotted ages versus depth for the Wyee Bay sediment core WB1C based on CIC and CRS modelled ^{210}Pb activity. A change to the depositional regime at the site during c.1972 to 1980 is indicated by a bimodal sedimentation rate (SR).

Table 3.2 Presence of 29 species of benthic diatoms as a percentage of samples analysed and maximum RA scores for WB1C (N_{core}, Max_{core}) n=33 and analogue samples ($N_{analogue}$, $Max_{analogue}$) n=34 (Central Coast dataset).

Species	Code	N_{core} %	Max_{core} %	$N_{analogue}$ %	$Max_{analogue}$ %
Benthic species					
Amphora ventricosa W. Gregory	Ampven	0.0	0.0	82.6	4.6
Amphora acutiuscula Kützing	Ampact	9.1	0.2	84.8	5.3
Cocconeis scutellum Ehrenberg	Cocscu	87.9	6.0	89.1	32.9
Cocconeis pseudomarginata Gregory	Cocpsu	93.9	2.7	56.5	7.2
Dimmerogramma minor (Gregory) Ralphs in Pritchard	Dimmn	72.7	1.7	50.0	1.2
Diploneis chersonensis (Grun in A.Schmidt) Cleve	Dipchr	90.9	8.8	63.0	19.4
Gramatophora spp. Ehrenberg 1839	Gramm	100.0	69.9	100.0	29.4
Gyrosigma cf. balticum	Gyro6	87.9	4.4	71.7	1.9
Melosira sulcata (Ehrenberg) Kütz *var. coronata* Grunow	Melslrd	100.0	27.8	60.9	23.9
Melosira sulcata (Ehrenberg) Kütz *var. radiata* Grunow	Melslcr	100.0	37.0	63.0	17.6
Paralia sp.	Paral	81.8	10.3	65.2	45.8
Navicula rhaphoneis	Navrha	39.4	10.1	93.5	8.4
Navicula yarrensis Grunow	Navyar	97.0	9.2	89.1	4.6
Navicula punctulata W Smith	Navpun	84.8	1.2	63.0	1.7
Navicula robertsiana Greville	Navrob	90.9	8.3	71.7	2.2
Tryblionella lanceola	Nitlan	66.7	12.6	89.1	7.5
Tryblionella littoralis (Grun. in Cleve & Grun.) Mann in Round	Trylit	81.8	2.4	54.3	2.9
Psammodictyon panduriformis (Gregory) Mann	Psapan	30.3	0.7	80.4	3.7
Nitzschia cf. hummi Hustedt	Nithum	84.8	0.7	37.0	0.5
Stephanopyxis turris (Grenville) Ralphs	Stptur	84.8	8.5	87.0	46.6
Surirella fastuosa (Ehrenberg) Kützing	Surfat	97.0	7.6	78.3	31.0
Synedra investiens Smith	Syninv	30.3	2.7	71.7	6.7
Synedra formosa Hantz	Synfor	97.0	1.4	69.6	1.2
Synedra hennedyana Gregory	Synhen	72.7	0.5	54.3	0.7
Thalassiosira eccentrica (Ehrenberg) Cleve	Thlecc	30.3	2.7	80.4	8.0
Trachyneis aspera (Ehrenberg) Cleve	Traasp	100.0	10.6	65.2	1.7
Planktonic species					
Cyclotella striata (Kützing) Grunow	Cycstr	93.9	6.2	100.0	27.0
Cyclotella choctawhatcheeana Prasad	Cyccho	90.9	5.6	73.9	6.1
Dictyocha fibula Ehrenberg	Dicfib	51.5	2.6	82.6	9.8

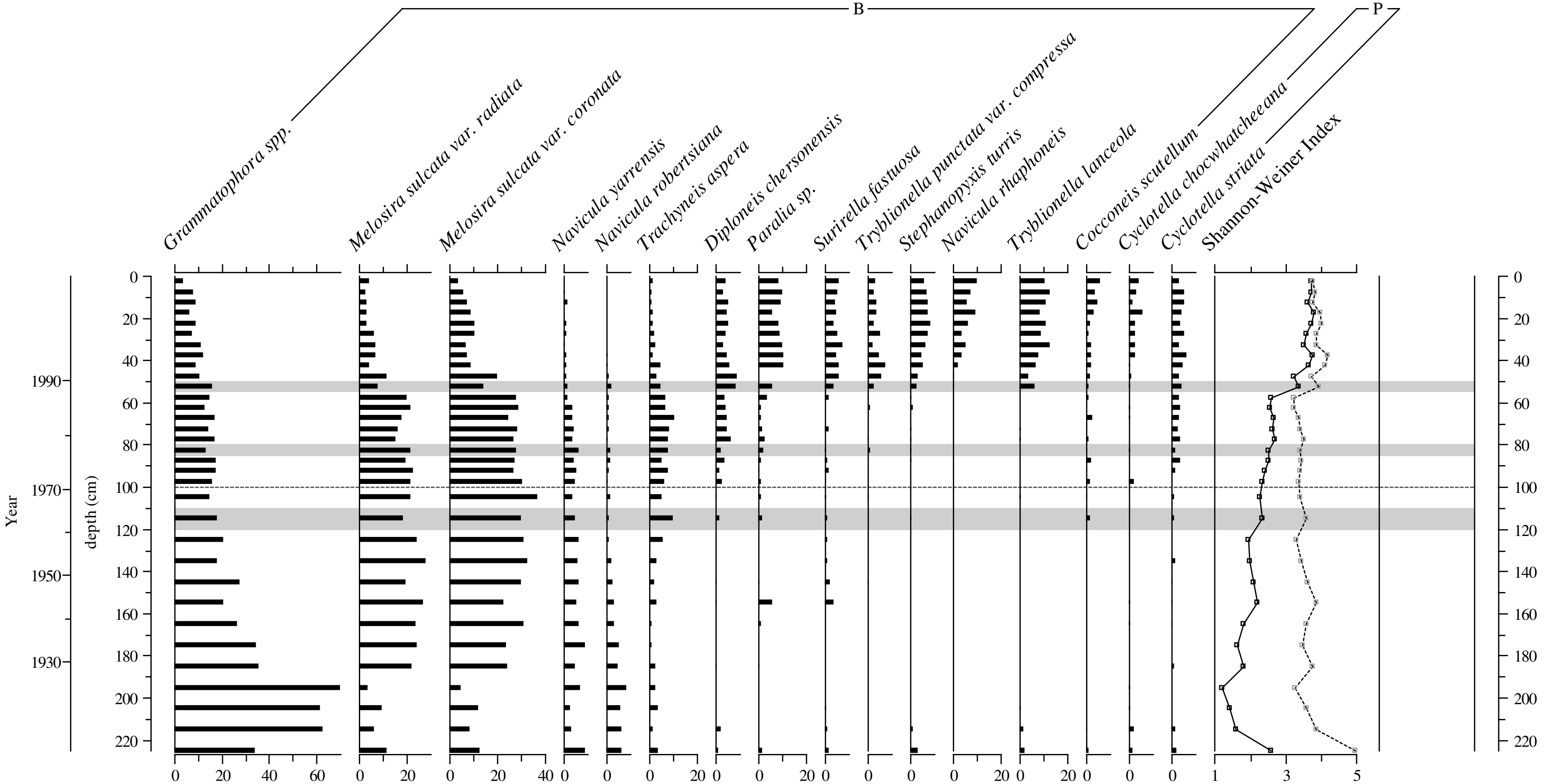


Figure 3.5a Downcore representation of the relative abundance of 16 most common species from WB1C. Grey horizontal bands denote CRS ages and errors around 1963, 1978 and 1989; dashed horizontal line separates 0.5cm (upper) and 1 cm (lower) sampled core intervals; P-pelagic; B-benthic; raw (solid line) and depth normalised (dotted line) S-W index values.

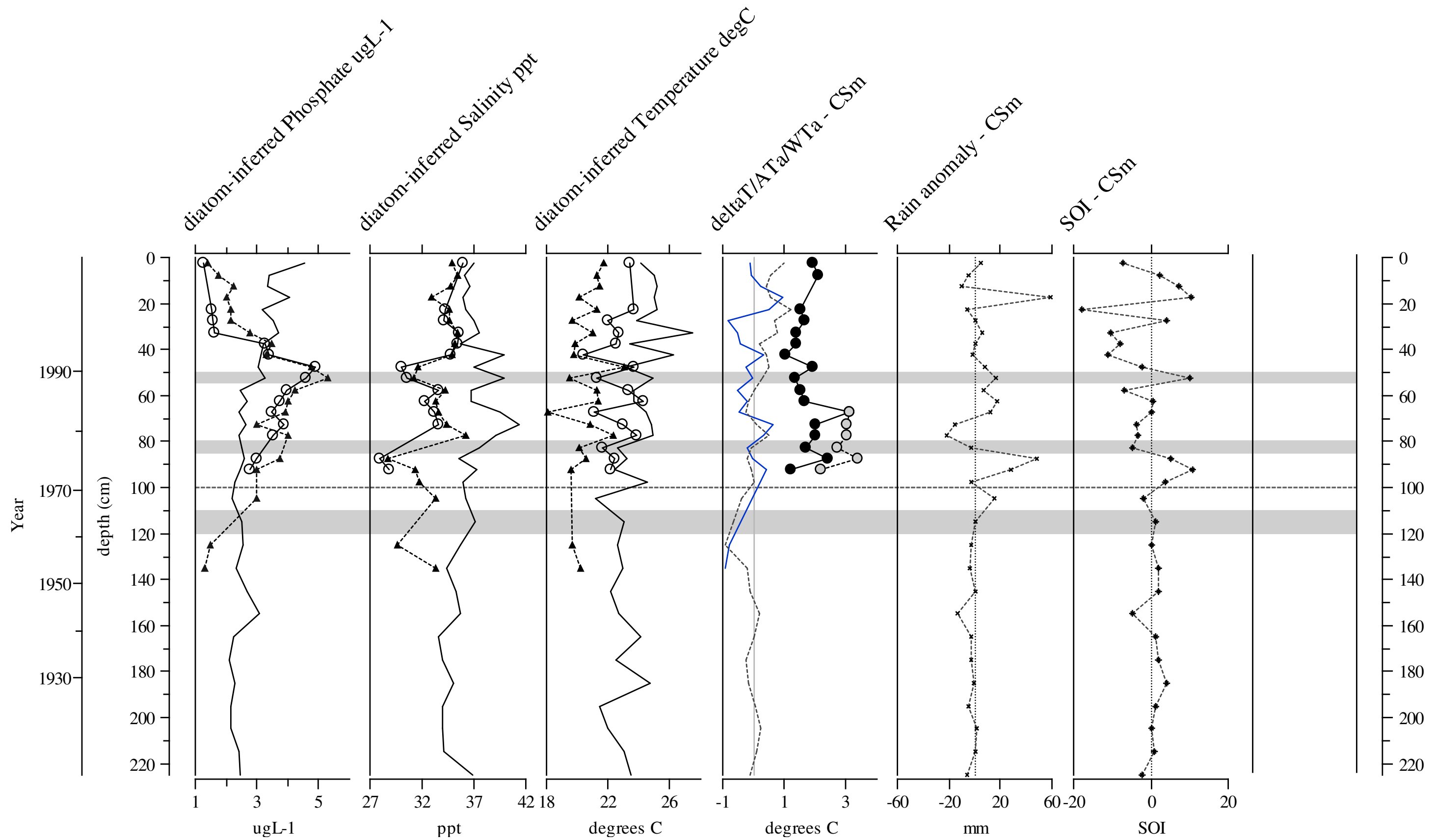


Figure 3.5b Diatom-inferred reconstructions for phosphate, salinity and temperature (solid lines) plotted against Wyee Bay water quality CSm (solid triangles) and lake CSm (open circles). Downcore CSm values for water temperature anomaly (WTa) (blue line), air temperature anomaly (ATa) (grey line), ΔT (black circles) & corrected site E1 data (grey circles); with seperate plots denoting calculated CSm rain anomaly and SOI values..

3.4.3 Combined Epibenthic and Fossil Data

When core and reference dataset were combined in a CA, Wallis Lake (WAL1 and WAL2) sites plotted nearer to core depth intervals 7-23 cm than all other reference locations (Figure 3.4). Differences between the core interval 20-23 cm and Wallis Lake samples, however, were statistically significant ($p<0.05$; average dissimilarity 72 %). Plots combining initial survey sites (2002-2003 samples) also showed that WB1C core surface samples (0.5-2.5 cm) were similar to Wyee Bay (sites WB3, WB4 & WB5) and Chain Valley Bay (sites CV4 and CV5) (Figure 3.6c,d).

3.4.4 Transfer function development, reconstruction and validation

Bi-plots of species and environment data are presented in Figure 3.7. Auto-forward selection in a CCA with all 10 environmental variables indicated that salinity, temperature, phosphate, NH3, silica and NOx were the environmental variables that explained the greatest proportion of variability within the reference dataset. Variance partitioning using only these six variables indicated that salinity (10.1%), phosphate (7.8%) then temperature (7.2%) explained the greatest proportions of independent variance in the dataset (Figure 3.8) with NH3, silica and NOx contributing between 5.3-6.9%. While interaction between covariables (2-variable tests) was highest for salinity (average 5.3%), covariable interaction (2-variable interaction) for the other 5 variables averaged 1.7%. A DCCA indicated that all variables were suitable for transfer function development except NOx. For the other variables, a minimum ratio (λ_1:λ_2) of 0.72 was determined for ammonia. The analysis demonstrates that no 1 or 2 variables dominated the dataset making reconstructions on any variable difficult to justify. As variance partitioning identified salinity, phosphate and temperature as the most dominant and potentially worthy of reconstruction, these variables were investigated further.

PLS and WAPLS produced better models (i.e. improved r^2, r^2_{boot}, RMSE, RMSEP values) compared to WA methods for salinity (+ 20%) and temperature (+ 12%, Figure 3.9; Table 3.2).

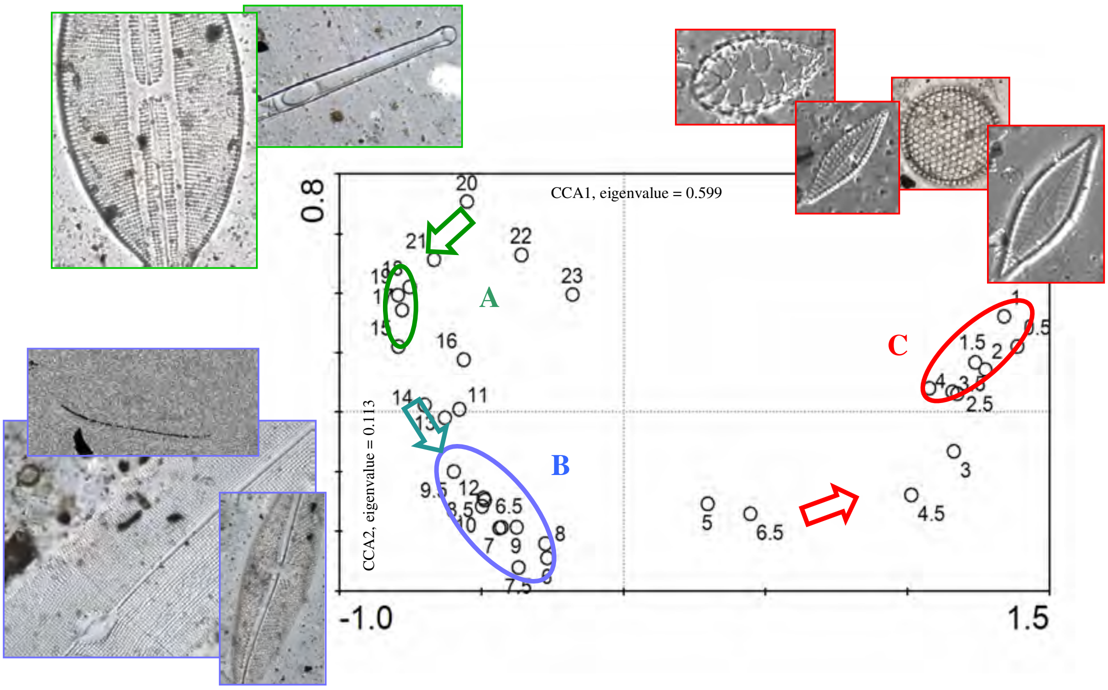


Figure 3.6 Plot of PCA scores for assemblage data for core WB1C with values indicating core slice depths. Periods of relative stability (circles) denoted by core depths across relatively small gradients and periods of change (arrows) denoted by larger gradients between adjacent depth slices. Each of the assemblage groups were dominated by species including (anti-clockwise from top-left) Group A: *Grammatophora* sp and *Navicula robertsiana;* Group B*: Tryblionella littoralis*, *Gyrosigma* sp7 and *Trachyneis aspera*; and Group C: *Navicula rhaphoneis, Stephanopyxis turris,. Tryblionella lanceola and Surirella globosa.*

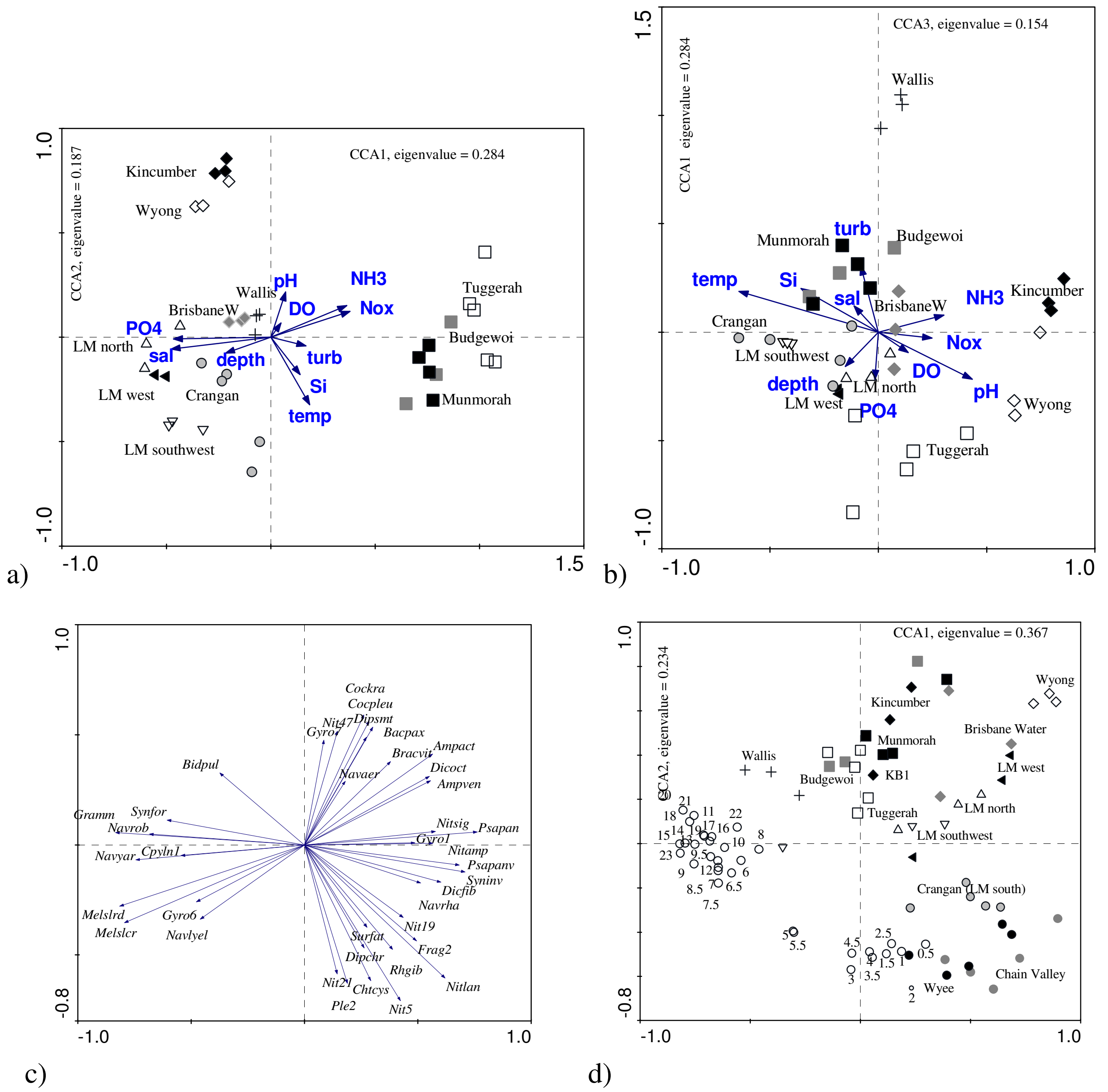


Figure 3.7 Scatter plots representing CCA scores of species and environmental variables for reference sites (Central Coast sites only) displaying principle axes a) 1 and 2 & b) 3 and 1, and CA for combined core, reference and sites from Chapter 2 (Ingleton and McMinn, 2012) as c) species and d) samples. Refer to Figure 3.2 for a key to symbols and Table 3.2 for species abbreviations.

Reconstruction standard errors (rSE) were ±1.0 for salinity, ±1.1 °C for temperature and ± 1.2 µg L^{-1} for phosphate. Plots of receiving bay and lake-wide CSm values for salinity, temperature and phosphate (1953-2003), diatom-inferred salinity, temperature and phosphate are presented in Figure 3.4. CSm values for air temperature anomaly, lake water temperature anomaly, rainfall anomaly and SOI are also presented. General trends in long-term water quality data most closely resembled transfer functions trends for PLS principle component 2 (PC2) for salinity and temperature. The salinity transfer function had better predictive ability than that for temperature.

The reconstruction for temperature was consistently offset (<1 °C) from real time data likely as a result of the monitoring site being located further downstream within the plume field (500 m) relative to the core site. Temperature predictions appeared to perform well relative to Wyee Bay temperatures over ~1970-1992 but the relationship was marred by high relative rSE values. Qualitatively, the relatively variable nature of the monitoring data across the 1980-1990s appears to be reflected within the reconstructed values (Figure 3.5b). A general trend of increasing temperature over time is predicted with some confidence with temperatures steady around 23 °C from 1910-1960s. Since the time of power station commissioning predicted water temperatures increased by ~2-3 °C compared to the receiving bay, lake-wide and air temperature increases of 1.63-1.80 °C , 0.2-0.4 °C and 0.9 °C, respectively. Accounting for rSE this equates to only ~0.5-0.8 °C estimation of increased temperature from the model. Diatom-inferred water temperature correlated significantly with CSm air temperature anomaly values (1910-2003) using PLS PC2 ($n=33$; $r^2=0.31$; $p<0.05$) but not for WAPLS PC2 ($n=33$; $r^2=0.04$; $p>0.05$.).

CSm ΔT ranged from 1.2-2.4 °C (equivalent 2.2-3.4 °C site E1 to HWC1 adjusted) across the period 1973-1982 (site E1 data), 1.4-3.1 °C from 1982-1989 (HWC1), and to 1.0-1.9°C from 1989-2003 (HWC1 and LMB7). Correlations between ΔT (1973-2003) and PLS or WAPLS modelled temperatures (n=21) were non-significant. Air, lake and receiving bay water temperatures were seasonally driven and all significantly correlated with each other ($p<0.05$). Regionally driven SOI, lake water temperature anomaly and air temperature anomalies did not correlate significantly with ΔT or receiving bay water temperature anomalies, indicating that Wyee Bay temperatures were driven by a more localised factor(s).

For salinity, predictions were relatively accurate for the most recent period (1992-2003), however, they diverged from measured salinity with increased depth (Figure 3.5a). The salinity model performed better over shorter time scales and generally appeared to follow modelled salinity with a 1-slice depth offset. Periods of relatively lower salinity coincided with periods of extended positive SOI and rainfall anomalies. Significant correlations for salinity with SOI (r^2= 0.15, n= 350; p<0.05) and salinity with lagged (1-month) rainfall anomaly (r2=0.20, n=350, p<0.05) were established. Generally, the salinity model only predicted the long-term increase in salinity for part of the core. Salinity increased over time since the 1960s and may be attributable to a greater proportion of negative (drier conditions) SOI than positive SOI for the period.

For phosphate, both WAPLS and PLS models for phosphate matched the generalised trend of increasing concentrations across 1953-1990 only (Figure 3.5b). Even for this period the model underestimated the phosphate concentration by a factor of 3-4. Thus, the model was considered to be a poor representation for phosphate and not discussed further. Changes in long-term phosphate concentrations from monitoring, however, are discussed in the context of anthropogenic pressures on the lake's environment.

Table 3.3 Calculated R^2, R^2_{boot}, RMSE and RMSEP values and reconstructed standard error ranges from PLS, WA and WAPLS models for log transformed salinity, temperature and phosphate based on the central coast reference set.

Bootstrapping n=100 Model	Variable	R^2	R^2_{boot}	RMSE (log)	RMSEP (log)	Recons. SE
PLS (linear)	Sal	0.94	0.86	0.02	0.04	± 1.05
	Temp	0.82	0.56	0.05	0.08	± 1.08 °C
	PO4	0.92	0.75	0.08	0.16	± 1.19 µg L^{-1}
WA (unimodal)	Sal	0.88	0.84	0.04	0.05	± 1.03
	Temp	0.67	0.47	0.07	0.09	± 1.07 °C
	PO4	0.84	0.75	0.11	0.15	± 1.18 µg L^{-1}
WAPLS (unimodal)	Sal	0.95	0.85	0.02	0.04	± 1.03
	Temp	0.83	0.59	0.05	0.08	± 1.06 °C
	PO4	0.90	0.77	0.09	0.15	± 1.19 µg L^{-1}

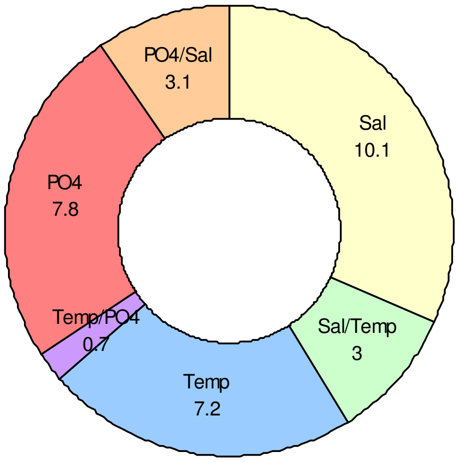


Figure 3.8 Relative proportions of independent variability for each variable and variation explained by two co-variables according to CCA analyses and manual forward selection.

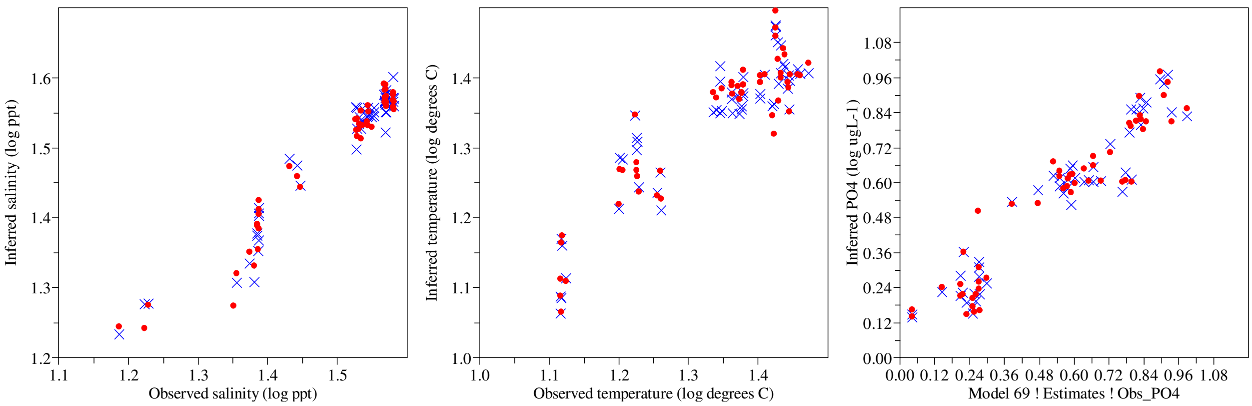


Figure 3.9 Plots of observed salinity, temperature and orthophosphate values versus PLS (x) and WAPLS (●) model inferred values (PC2) from the central coast reference dataset.

3.5 Discussion

3.5.1 Environmental changes in the receiving bay environment

Shifts in the assemblages of benthic diatoms in the receiving water embayment of Wyee Bay coincided with power station operational changes and changes to the temperature regime at the core site. While the model and reconstruction did not accurately describe small temporal-scale temperature variability, over longer time scales, the model indicated that water temperatures in the receiving bay were 2-3 °C warmer 1989-2003 compared to 1910-1960 (Figure 3.5). Prior to the power station discharge, temperatures were stable around a mean of ~23 °C (21-25 °C range) and the diatom flora was dominated by species *Grammatophora* spp. and *Melosira sulcata*. Optima for these species were determined to be relatively cooler at ~21 °C according to data obtained from estuaries of the south-east coast (Chapter 4).

Both monitored and modelled temperatures post-commissioning were greater than temperatures during pre-commissioning times. The diatom-inferred temperature model, however, did not peak during the period of peak power station output (~1978). Assemblages during the most recent period (1989-2003) were dominated by the thermal plume indicator species *Navicula rhaphoneis* (Chapter 2 – Ingleton and McMinn, 2012) and *Amphora acutiuscula* Kützing and are the same species associated with other central coast sites exposed to thermal plumes with temperatures of >25 °C (Chapter 4). Wyee Bay temperature regime at the core site changed to ~25 °C (i.e., from 23-27 °C) by 2003 (Figure 3.5).

For salinity, estimation of salinity in pre-power station times either from models or relative to indicator species was problematic. While the model performed well over small temporal scales and was relatively accurate for the most recent period, trends over the whole core and estimates of salinity over 1910-1950 were difficult to establish. While declining abundances of *Cyclotella* were indicative of changes to predominantly freshwater inflows for the Hawkesbury River (McMinn et al., 2004), increases in *Cyclotella* species occurred across a period of increasing salinity (1953-2003) in Wyee Bay. A decline in the marine species *Grammatophora* spp. (Witkowski et al., 2000), but increase in *Paralia* sp. in recent times adds further complexity to the lake's salinity story when attempting to infer system changes based on species compositions.

The mixed provenance of species contained within the core slices may be a result of both allochthonous and autochthonous diatoms contributing to the fossil record at the site (Vos and de Wolf, 2003). Factors such as light regimes and stratification are also likely to contribute to the proportions of planktonic relative to benthic species. The presence of species indicative of a wide salinity range within sediment slices representing ~1-2 years suggests high salinity variability over small temporal scales. In comparison, the assemblage as a whole was assemblages were relatively consistent from 1989-2003. This may indicate that the 'variable' salinity regime was relatively consistent over this time period.

Variability in salinity appeared to be driven by a suite of anthropogenic and climatic factors working across a range of temporal and spatial scales. Generally, salinity in Lake Macquarie is influenced by freshwater inputs from catchment inflows, evaporative loss and a baseline value maintained by a restricted but permanent connection with the open ocean (Floyd, pers. comm.). Increasing salinity over time for the lake is likely associated with a reduction in effective precipitation for the lake associated with a period of negative SOI. Catchment degradation and changes to freshwater inflows (SPCC, 1983; LMCC, 1997) may account for changes in the relative abundances of benthic versus plaktonic taxa. After heavy rain, flows can be delivered to estuaries more quickly than would otherwise occur from vegetated and less developed areas (Harris, 2001). How this alters the salinity regime of the lake is uncertain. It is hypothesised, however, that the expediated flow of freshwater from the catchment to the estuary may invoke a lake condition whereby stratification is sustained for longer periods. Brackish planktonic species are sustained within the water column while saline conditions occur at depth, and both are then co-represented within the fossil record.

Both predicted and long-term monitoring temperature and salinity data varied independently of each other with time (Figure 3.5). This indicated that although there is likely to be some relationship between salinity and temperature, the variables appear to be acting as independent drivers of species assemblage changes within these datasets. Over a period where salinity describes the reconstruction reasonably well temperature is likely to perform relatively poorly and vice versa.

The relationship between species and key variables is further complicated by additional environmental variables that contribute as underlying secondary drivers of diatom distributions. Phosphate concentration in the receiving bay and broader lake varied independently of salinity and temperature over inter-slice time scales. Increased volumes of sewage discharged to the lake increased nutrient levels until 1992-1994 (Eyre, 2005), when flows were redirected to the ocean (AWACS, 1995). The species *Cyclotella choctawhatcheeana* Prasad increased in abundance after this time. This particular species has been previously associated with anthropogenically affected sites but not necessarily high nutrient environments (Weckström and Juggins 2006). *Cyclotella choctawhatcheeana* was, however, absent from the deepest sections of the core when phosphate had been generally lower (<2 μg L^{-1}). Since the redirection of sewage, point discharges of nutrients have been replaced by more diffuse sources (AWACS, 1995) such as urban runoff (LMCC, 1997). These considerations highlight the high variability that can be experienced within estuaries and hence the challenges of palaeolimnolgical applications in these environments.

3.5.2 Temporal shifts in diatom assemblages and diversity

While the model did not provide a downcore temperature signal responsive to small-scale temporal changes in plume temperatures at the site, distinct assemblages were associated with various pre-power station and post-power station periods. Stable assemblages covering periods on the scale of decades were interrupted by variable assemblages and relatively rapid shifts (years to a decade) to a new assemblage and periods of relative stability. These shifts are coincident with changes in the operational period of the Vales Point Power Station that is likely associated with changes in the receiving bay environment that includes, at least in part, changes to the bay's temperature regime. Potentially the observed changes in assemblages may have been associated with a more complex change in several co-variables. The diatom-temperature "signal" observed at the site and preserved in the fossil record (<2-2.5 °C) may simply have been too small to adequately delineate thermal plume temperature as the main driver in assemblage variability alone.

The stable period of 1930-1960 was dominated by abundances of *Navicula yarrensis, Trachyneis aspera*, *Grammatophora* spp., *Navicula robertsiana* Greville and *Melosira sulcata.* Commissioning of the Vales Point Power Station in 1963 provided the first thermal discharges to the bay and a shift in benthic assemblages was observed, with the first appearance *Trachyneis aspera*, *Diploneis chersonensis* and *Cyclotella striata* (Figure 3.4). By the time regular monitoring was initiated in 1973, a ΔT of ~2-3 °C (near Mannering Point) already indicated a shift in the bays temperature regime. A trend towards warmer than average regional air temperatures had also commenced (Figure 3.5).

An increase in the number of smaller species dominating the flora occurred around 1989. The plume indicator species *Navicula rhaphoneis* (Chapter 2 – Ingleton and McMinn, 2012), *Tryblionella lanceola*, *Stephanopyxis turris*, *Cocconeis scutellum*, *Surirella fastuosa*, *Paralia* sp., and the planktonic *Cyclotella choctawhatcheeana* either first appeared or increased in their relative abundance. This change coincided with a reduction in the power station's output capacity by ~40%, a reduction in mean ΔT of ~0.5-2 °C and general exposure of the benthos to elevated temperature at the core site.

A shift to a greater relative diversity across c. 1989 indicated a change in the receiving environment which may also be attributed to temperature. Generally, for marine organisms, increases in ambient temperatures invoke increased growth and development to a threshold point above which rates decline (Mustard et al., 1999). A decline in ΔT values may have induced a positive response in diatom diversity for the bay. Warmer regional air temperatures, lower nutrients (Eyre, 2005) and reduced heavy metal loads from fly ash (Peters et al., 1999b), however, may have provided additional mechanisms contributing to increased diatom diversity at around the early to mid-1990s.

From the stable assemblages observed it is possible that the continued presence of a thermal plume would be a direct result of a relatively more stable environment in comparison to ambient or pre-discharge periods. Even though temperatures in the bay are consistently elevated, seasonality within the discharge temperature signal is maintained (Chapter 2 – Ingleton and McMinn, 2012). Water temperatures are more variable as the presence of the plume increases the diurnal and annual temperature ranges by up to 5-6 °C. Thus, plume assemblages may contain species resilient to greater temperature variation than those in other embayments or prior to thermal discharges commencing. The resilience of species could be derived from the Weighted-Average tolerances or the temperature ranges over which they occur with some further analysis.

3.5.3 Long-term temperature trends and pre-power station conditions

Waters of the coastal ocean over Australia's south-east continental shelf have warmed at a rate of ~0.202 °C decade^{-1} (Thompson et al., 2009) with strengthening flow of the East Australian Current (Ridgway and Hill, 2009). This is turn is likely to have implications for local climate and estuaries (Gillanders et al., 2011). The regional air temperature and water temperature anomaly data support the idea or a warming trend for the waters of Lake Macquarie. While benthic diatom species such as *Navicula rhaphoneis* may be indicative of the extreme variability of plume temperature, long-term climate-based temperature changes might better be represented by other species. *Navicula robertsiana* and *Navicula yarrensis* steadily declined and *Diploneis chersonensis* steadily increased in relative abundance as regional temperatures increased (Figure 3.5).

Changes in the receiving bay environment during the pre-power station period were also observed ~1925-1930 (Figure 3.5). The assemblage was generally dominated by *Grammatophora* spp. (RAs >30%). Mechanisms for change during this period are difficult to attribute to any particular environmental factor with the absence of water quality data prior to 1953. However, previous studies have attributed metal contamination in the sediments to power station operations and discharges from a lead-zinc (Pb-Zn) smelter (Peters et al., 1999a; Olmos and Birch, 2010) in the lake's north. In Mannering Bay (Peters et al., 1999b), situated downstream of the Vales Point ash dam and upstream of Wyee Bay, enrichment (>2-3x background) of selenium (Se) commenced around 1937-1956 prior to the power station. Se has also enriched in Wyee Bay sediments (Roach, 2005) and thus had potentially contributed to assemblage patterns in the receiving bay from this time. Some metals (i.e., cadmium, Pb and Zn) have been shown to drive changes in the distribution of benthic invertebrates (Simpson et al., 2005) elsewhere in the lake and are also likely to have been a contributing factor to benthic diatom distribution over time. Downcore changes in diatom assemblages relative to sediment metals concentrations are yet to be examined.

3.5.4 Implications for lake management and further work

While little is known about diatom species and assemblage preferences/tolerances within Australian coastal waters, the data presented here contributes new information on the knowledge of benthic species for this part of the NSW coast. The data provided diatom preference data across gradients of 12.1-31.6 ºC for temperature, 14.4-37.4 for salinity and 0.1-9.0 µg L^{-1} for phosphate. For salinity the number of sites was skewed towards higher salinities with a (median 34) compared to temperature and phosphate where ranges and medians indicate values were relatively more normally distributed. It is likely that additional sampling across greater spatial and temporal gradients is required to provide an improved representation of the true range of species for this section of the Australian coast. This could potentially improve diatom-inference models.

The estuaries of the NSW central coast including Lake Macquarie are considered to be highly modified (Digby, 1998; NLWRA, 2001) and have been exposed to a range of anthropogenic pressures in recent times. Thus, the diatom history in these systems is likely to be complex. Palaeolimnology in estuaries is problematic and not applicable in all situations. Preferably, pristine or largely unmodified estuaries would be sampled for a reference dataset where significant anthropogenic pressures are minor or absent."

It has been demonstrated that changes in diatom assemblages within a bay exposed to a thermal plume are attributable to temperature regime changes associated with phases of power station operations. Other factors, however, also correspond with periods of assemblage change may and are likely to have contributed to the distribution of species over time and can not be ruled out. In the absence of controls the existing dataset is unable to delineate those assemblage responses specific to the receiving water bay from those common to other sites and assemblages within the lake.

One way of reducing model errors may be to increase the size of the dataset (Saunders et al., 2008). In the current study, sampling was targeted at sampling from lakes within the region, including sampling mud-basins of similar estuary-type and latitude to that of the receiving bay. Although the ranges of salinity and temperature sampled for the reference datasets covered the expected ranges, the distribution of sites was not evenly distributed along these gradients. A greater proportion of sites were represented at the higher salinity and lower temperature ends of the gradients sampled. Thus, an expanded reference dataset providing an increased sample density evenly distributed across a range of salinity and/or temperature gradients may help improve the confidence and sensitivity of the models.

Reference datasets should be tailored to adequately cover the range of the variable of interest. Temperature inference models can become problematic when they encompass only the natural levels of temperature variability and not extremes (Anderson, 2000). Temperature-assemblage gradients may be overridden and the diatom inference models become unreliable when other variables dominate (e.g., pH, in Bilger and Hall, 2003). Although an extreme artificial temperature gradient was sampled, the sample size was small and only relative to a single thermal discharge location.

The study made the most of validating the reconstructions with monitoring data. Such relative consistency in monitoring data within systems is rare, however, this study highlights its significance for palaeoecological reconstructions for validation of reconstructed values. While the CSm values determined were a “time-averaged” water-quality value calculated for a comparison against the equivalent “modelled” value for each core sediment intervals, these were determined from surface water samples only. Depth averaged values of the environmental variables may provide an improved correlation with diatom-inferred values but were not explored here.

A palaeolimnological analysis of cores from control locations within the lake together with a relatively pristine estuary elsewhere within the region would provide data for before, after, control and impact comparisons. Combined with heavy metal profiles, this would assist validating assemblages representing pre-industrial, pre-power station and post power station periods, providing a more comprehensive assessment of thermal plume effects.

Species preference information did not help in attempting to understand the long term changes in salinity. Modern assemblages are complex as they are exposed to a variety of competing anthropogenic pressures in addition to natural ones. This was observed for the most recent period of deposition where species with competing preferences for salinity (i.e., both freshwater and marine) were represented in the fossil record. The reconstructed temperature and diatom record indicated that power station operational changes driving changes in the plume regime may be responsible for long term shifts in assemblages and species diversity within the bay. This highlights the potential value of diatoms as powerful tools for identifying temporal changes in estuarine ecology due to anthropogenic activities.

3.6 Conclusions

The work conducted here attempted to establish the pre-condition and baseline water quality values for an embayment receiving thermal discharges from a power station. Model predictive ability was generally poor for temperature over short time scales when compared with long-term monitoring data. Over longer-time scales (decades) the model performed relatively well and indicated that temperatures were likely to have been 2-3 °C cooler preceding power station commissioning than in 2003. Assemblage and environmental monitoring data indicated that power station operational changes and the resulting shifts in water temperature regimes appeared to be responsible for shifts in assemblages and species diversity indices within the receiving water bay.

For diatom-inferred salinity, the model performed most accurately over 1992-2003. Generally, the model performed well and predicted the changes in inter-slice salinity variation associated with SOI and rainfall. A trend of increasing salinity since the 1950s was not described by the diatom-inferred salinity model. Reconstructed salinity did not appear to accurately establish pre-power station salinities. Although the salinity range covered within the reference dataset was adequate, data were somewhat skewed with a dominance of sites with generally higher salinities.

Expanded reference datasets over greater spatial scales and broader ranges of the key environmental variables may provide for improve model performance and reduced reconstruction errors. The study conducted here demonstrated that multi-assemblage and palaeoecological techniques using diatoms are powerful tools that can be applied to identifying anthropogenic induced changes in estuarine ecology. Palaeolimnology in estuaries is problematic and not possible to achieve in all situations. For development of reference datasets the use of pristine or unmodified systems is ideal to avoid additional complexities to the diatom-environment response expected for modified systems.

4. Diatom-Temperature Transfer Function

Sensitivity to reference dataset sample design and implications for reconstruction of a temperature history for an embayment receiving cooling water from a power station.

Abstract

Sampling design is a key consideration for the development of reference datasets in diatom-inference modelling, as the spatial distribution of sites relative to environmental variables, may have significant implications for model performance. Benthic diatom and environment data for a nested (sites and lakes) reference dataset was developed along a latitudinal gradient (26.4 – 37.3 °S) across south-east Australian estuaries. Sensitivity of the dataset, diatom-inference models and a temperature reconstruction was tested by performing iterations on different forms of the dataset varied by the numbers of sites, species and taxonomic resolution. Latitude, salinity and phosphate were consistently responsible for the greatest proportion of independent variability and were the main drivers of gradients in each of the datasets. With latitude removed temperature became a dominant variable that could be used for model development. For datasets reduced to a genus level resolution, salinity replaced latitude as the most dominant environmental variable. Models generally performed better when reference datasets were spatially structured (nested) or contained a greater number of species and covered a greater geographical range. Latitudinal based datasets improved temperature-model performance relative to a locally-based reference dataset. They also resulted in improved reconstruction standard error values for species-based datasets. Only for scenario nTL1 (nested) did the correlation coefficient approach being significant ($p<0.05$; n=28). The study demonstrates the limitations of reference datasets to specific applications. For contemporaneous assessments, while some economy may be achieved by smaller sample sizes over an appropriate gradient, genus level analyses were considered inadequate for diatom-inference modelling in this instance. The dataset builds on previous benthic diatom work for south-east Australian estuaries and further demonstrates their potential development as large scale bioindicators of system health.

4.1 Introduction

Diatoms are widely used in studies to understand environmental change in aquatic systems, as they are pervasive and cosmopolitan in nature, and sensitive to a range of environmental factors (Round et al., 1990; Reid et al., 1995). Similar to other organisms, diatoms display a temperature preference along natural thermal gradients. Their biogeographical distribution has been associated with temperature in oceanic systems (Esper et al., 2010; Crosta et al., 2005; Zielinski and Gersonde, 1997), natural thermal springs (Boylen and Brock 1973; Vinson and Rushforth, 1989), latitudinal (Pienitz et al., 1995), geographical (Potapova and Charles, 2002; Weckström et al., 1997) and longer-term climatic changes in water temperature (Snoejis, 1990; Cremer et al., 2001).

In the context of change, baseline data on the spatial distributions of species and their ranges are invaluable to understand changes associated with temperature shifts (i.e. Tasman Sea warming, Cai et al., 2005). For Australia, a 0.7 °C increase in ocean temperatures (Thompson et al., 2009) since the early 20th century is predicted to reach 2.5 °C by 2100 (Lough, 2009). For this reason, baseline data is required for effective management of anthropogenic induced change including pollution, to provide information on the pre-industrial condition of environmental systems. For Australian estuaries, environmental datasets are often limited, lacking adequate temporal perspective, or completely absent (Saunders and Taffs, 2009).

In the absence of long-term water quality data, palaeolimnological data derived from fossil diatoms may be used to determine the direction and nature of anthropogenic induced change in systems (Taffs et al., 2008). This technique is considered among the most powerful for identifying suitable reference conditions within aquatic systems (Dixit et al., 1992). For understanding anthropogenic effects in contemporaneous environments, bio-indices based on the diversity or variability of assemblages are among the most common indices developed for ecosystem health assessments (DelaCruz et al., 2006). Diatom based indices based on multiple-taxa (Potapova and Charles, 2002; Kelly, 1998) as well as species specific indices and key environmental factors (autecological) (Van Dam et al., 1994; Potapova et al., 2007) have been developed widely for Northern Hemisphere systems.

In Australia, the development of similar tools has focused on freshwater systems. While limited work has utilised diatoms (Reid et al., 1995; Growns and Growns, 2001), effort has favoured indices based on macroinvertebrates (Chessman, 1995; Turak et al., 1999). In estuaries, the applications of bio-indicators for broadscale health assessments are relatively recent. Current programs for Monitoring Evaluation and Reporting (MER) in coastal environments in Australia combines the use of traditional water quality parameters (chl-a and turbidity) and suitable guidelines (ANZECC & ARMCANZ, 2000), with biologically based assessments of seagrass, mangroves and saltmarsh distributions and fish assemblages (NSW State of the Environment, 2009).

The spatial scale over which monitoring programs are developed and implemented varies depending on their purpose (Lovett et al., 2007). (i.e. broadscale health assessments versus discharge licensing). For management, the use of biological indicators may be considered labour intensive, specialised and costly compared to traditional water quality assessments. One means of achieving reduced costs may be associated with limiting the number of sampling sites and/or, where appropriate, a reduction in the taxonomic resolution. For example, the Australian River Assessment System (AusRivAS) program provides a rapid assessment of river health using a calculation of an index based on taxonomical identification of macroinvertebrates (family level) and river water quality (Chessman, 1995; Turak, 1999).

In palaeoecology the majority of effort has focused on freshwater systems and the inference of salinity, nutrients, pH and/or temperature. While many diatom-temperature transfer functions have been reported (Anderson, 1993; Pienitz et al., 1995; Weckström et al., 1997) some authors consider them to be only reliable in applications where temperature is the driving environmental factor (Anderson, 2000). Where other variables dominate, (i.e. pH), the relatively weaker temperature-assemblage gradients may be overridden and temperature models in these cases may become unreliable (Bilger and Hall, 2003).

Diatom-based models developed for south-east Australian systems (Tibby et al., 2003; Tibby and Reid, 2004; Tibby et al., 2007) have focused on diatom-salinity, phosphorus and pH relationships in freshwater systems. By comparison their use in estuaries has generally been underutilised (McMinn et al., 2004) but are increasingly being applied (Trabajo and Sullivan, 2010; Cooper et al., 2010; Tibby and Taffs, 2011). Recent work in the south-east of Australia has applied palaeoecological techniques to examine anthropogenically induced change in sub-tropical (Taffs et al., 2007; Logan et al., 2011; Logan and Taffs, 2011) and temperate estuaries (Saunders et al., 2007, 2009, Saunders, 2011; Ingleton and McMinn, submitted). The use of a diatom-temperature inference model has also been reported in relation to a power station discharge (Chapter 3 - Ingleton and McMinn, 2012). Generally, reference datasets for models have been localised and of a relatively limited geographical range (<500 km). In comparison to European diatom databases (Weckström and Juggins, 2006) Australia has a relatively large coastline and variable estuarine typology (Roy et al., 2001; OzCoasts, 2009). Only recently has a diatom dataset covering Tasmanian and Victorian estuaries and a salinity model been published and is the first broad scale assessment of its type for Australian waters (Saunders, 2011).

The present study conducted here builds on work for the south-east Australian coast (Saunders, 2011) extending the geographical coverage ~1200 km further north and overlapping with work on the NSW north coast (Logan and Taffs, unpub.). This means for the first time, diatom and water chemistry data are available for the entire south-east Australian coastline (2.5-3K km) from temperate Tasmania and Victoria to sub-tropical southern Queensland. Although a number of environmental variables are likely to be adequate for the development of diatom-interference models, the main aim of this chapter was to develop a diatom dataset across a latitudinal temperature gradient. The main aim of the dataset was to test for improved performance of the temperature transfer function and reconstruction of a temperature history for Wyee Bay, Lake Macquarie. To test transfer function sensitivity, the reference dataset was also partitioned in six different ways and the various multivariate analyses applied to each subset.

4.2 Background

Sea levels in south-eastern Australia began to rise towards the end of the last glacial period (~18 ka years ago) and stabilised ~12-6 ka years ago (Thom and Chapel, 1975). Since that time, an abundant near-shore sand supply and accreting coastline has provided a stable sedimentary environment that has persisted for >4000 years (Thom, 1974). Formation of many of the estuaries along the Australian coast occurred as a result of the impoundment of water bodies behind barriers of marine sand (Roy and Peat, 1973).

Estuaries of the region (26.3–37.2 °S) are sub-tropical to temperate (Digby, 1998) with annual average daily maximum air temperature of between 18-24 °C (BOM, 2011). The coast is exposed to a high-energy wave climate dominated by south-easterly swells generated from within the Tasman Sea (Thom et al., 1973; Wright, 1976). Thus, the estuaries are termed wave-dominated systems (Roy et al., 1980). They range from lakes with permanently open but small restricted entrances to tidally dominated river-systems with back-barrier lakes/lagoons as off-channel embayments in their lower reaches (OzCoasts, 2009). Approximately 25-30% of NSW estuaries are relatively small lakes or lagoons with small catchments and intermittently closed/open (ICOLLS) connections to the ocean (Gale et al., 2008).

Since European settlement many coastal ecosystems have been highly modified as a result of increasing population and pressures associated with coastal development (National Land and Water Resource Audit, 2001). The ecological status of estuaries around the main metropolitan centres (e.g., Melbourne and Sydney) are generally classified as “considerably” to “moderately” affected when compared to near-pristine systems. For example, Wonboyn and Smiths lakes (Figure 4.1), which are more than 100 km from the nearest metropolitan area, are considered to be only “slightly” affected (Digby, 1998). The level of development within systems is also spatially variable. Lake Wooleweyah and Pambula Lake are

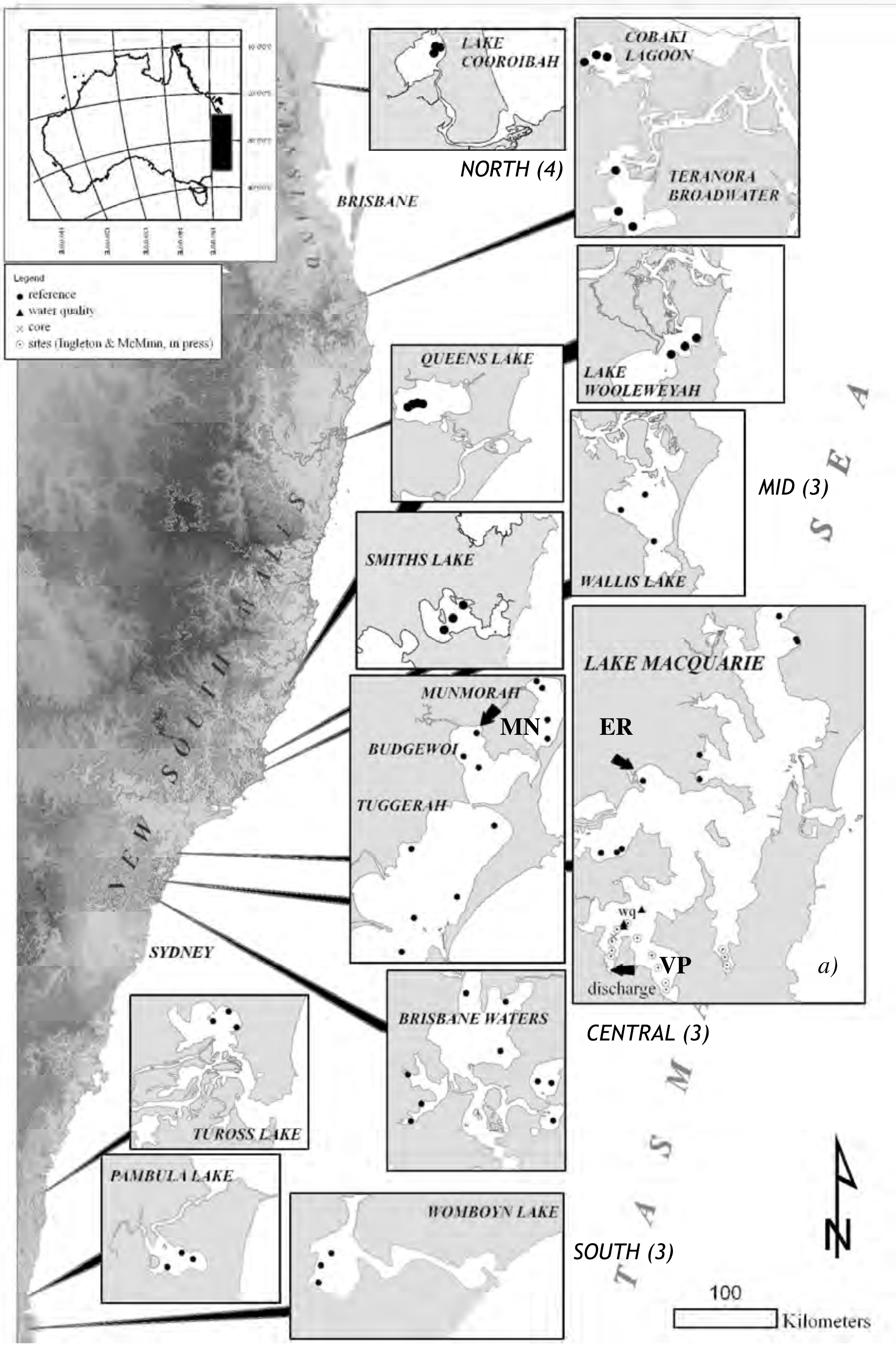


Figure 4.1. Location of lakes/lagoons and sampling sites of the south-east coast from Noosa to Eden, and a) Lake Macquarie, Australia. Arrows indicate power station discharges at Vales Point (VP), Eraring (ER) and Munmorah (MN).

characterised by modified upper catchments but possess lower estuarine areas bordered by nature reserves and national parks.

Lake Macquarie is the largest and deepest wave-dominated (back-barrier) coastal lake in New South Wales (NSW, Roy et al., 1980) covering an area of over 110 km^2 and maximum depth of 14 m (Figure 4.1). The lake experiences limited tidal exchange due to a restricted entrance at Swansea (<1% per tidal cycle) (Spencer, 1959). Many of the upper embayments provide ideal conditions for the deposition of finer (<63µm) sediments and are mud-dominated (Roy and Peat, 1975). The catchment of Lake Macquarie is moderately developed and its ecological status is considered as moderately affected (Digby, 1998). Historically, the lake has been subjected to significant industrial, urban and rural development and has been impacted upon by heavy metals and other pollutants (Olmos and Birch, 2010). Several of these pressures have reduced in recent years with concentrations of metals and nutrients in decline (AWACS, 1995; Roach, 2005). Issues associated with metal contamination, however, remain a legacy for the lake environment.

Due to the proximity of coal reserves the shores of the lake have played host to power stations since the 1950's, which in turn utilise lake water for cooling the coal fired turbines. Vales Point power station, located in the south-west section of the lake, has been in operation since 1963 and currently operates at a capacity of 1320MW (Figure 4.1a). Lake water is drawn into the station on the western shore of Chain Valley Bay and is discharged at the southern end of Wyee Bay at a rate of up to 50 m^3s^{-1} and a licensed maximum of 35°C (limited max 37.5°C). Satellite imagery has shown that the heated water plume consistently extends beyond the immediate confines of the receiving water bay (Wyee Bay) and at times extends as far as the power station intake (Chapter 1). As a result, under certain conditions benthic environments north of Vales Point are exposed to elevated temperatures of between 0.5-1°C above seasonal ambient temperatures.

4.3 Methods

4.3.1 Site Selection

To provide a dataset that represented a relatively even distribution of sampling effort, data from four lakes in the north and three lakes in each of the mid-north, central and far southern coastal settings of NSW (Figure 4.1), sampled from 2007-2010, were obtained (3-4 sampling sites per system). This dataset represented a replicated nested sampling design across the geographical range, and was termed the nested Temperature-Latitude dataset (nTL; n=40). Sampling was designed to encapsulate a “natural” temperature gradient induced by changes in latitude across the region (7.1 - 8.7 °C range – this study).

Wave dominated coastal lakes of estuaries with restricted entrances but predominantly open to the sea (Digby, 1998) were targeted as were systems of only moderate to slightly affected ecological status. This system type was selected to replicate sampling in lakes of similar morphology (mud-basin) and hydrology (limited tidal exchange - wind dominated) to that of Lake Macquarie. Ideally, systems targeted for sampling were near pristine. The number of systems with this typology in the northern region, however, was limited and sampling of modified/affected systems was unavoidable (Table 4.1). Sampling was also targeted to acquire predominantly muddy sediments in water depths less than 4 m.

Previously, data collected from sampling sites across NSW central coast lakes (Chapter 2) and Lake Macquarie sites 2002-2003 (Chapter 1) were combined (n=51) for the development of diatom-inference models and reconstruction of a water quality history for Wyee Bay. Wyee Bay receives a thermal discharge from Vales Point Power Station and sites sampled from 2002-2003 provided data on benthic diatom assemblages across an anthropogenically induced temperature gradient of 6-12 °C. An extended diatom dataset containing species and environmental data from all sites sampled (n=80) across all 13 coastal lakes/lagoons between Noosa (26.4 °S) and Eden (37.3 °S) (2002-2010) was also created and termed the ‘extended Temperature-Latitude’ (eTL) dataset.

Table 4.1. Estuary morphology and condition data adapted from OzCoasts 2009 based on Digby (1998) and NLWRA (2001).

	Cooroibah	Cobaki - Teranora	Wooleweyah[1]	Queens	Wallis	Smiths	Crangan Bay	Tuggerah	Brisbane Water	Tuross	Pambula	Wonboyn
	North			Mid			Central			South		
Catchment area km^2	84	11	20	60	13	46	78	82	21	18	28	35
Open water km^2	64	23	24	28	10	9	11	79	29	16	3	6
Entrance												
Development												
Condition												
Conservation Value												
Ecological status												

KEY
- Entrance: unres/restricted
- Development: sparse/moderate/high
- Condition: unmodified/mod/extreme
- Conservation Value: high/moderate
- Ecological status: slight/mod/considerably

[1] data for sub-catchment only in Foley & White (2007) and Lancaster (1990)

4.3.2 Sediment sample and environmental data collection

Sediments were collected using a modified passive gravity corer and removable 500 mm lengths of 74 mm diameter clear polyvinyl chloride (PVC) tubing. Cores were extruded on site and 5-10 g wet weight sediment from the top 0.5 cm of the core was transferred into sterile 50 mL high density polyethylene (HDPE) centrifuge tubes. Samples were transported to the laboratory and stored in the dark at 2-4 °C prior to slide preparation. Sampling the top 0.5-1 cm of surficial sediment is thought to provide a spatial and temporally integrated sample of the diatom communities at a site (Lim et al., 2007).

Dissolved oxygen, pH, temperature, salinity and turbidity data were collected at each site using a Yeo-Kal 612 Water Quality Analyser (YeoKal Electronics, Australia) at the surface (0.2 m), 0.5 m, 1 m and at 1 m intervals to the lake bottom. Water samples were obtained from a depth of 0.2-0.5 m using a closing bottle sampler (1.5 L Niskin, General Oceanics, USA) and then filtered through 0.45 µm syringe filters to sterile 30 mL vials and frozen at -4 °C. Water samples were analysed for dissolved phase nutrients (ammonia, oxidised nitrogen, orthophosphate and silicate) using a Lachat QuikChem 8000 (Hach Company, United States of America) flow injection analyser. Quantitation limits were 5 µg L^{-1} for silicate and 1 µg L^{-1} for other analytes.

Variability in environmental parameters for all lakes was examined using available longer-term datasets from the NSW Office of Environment and Heritage (OEH) Coastal Eutrophication Risk Assessment Tool (CERAT), South East Water Quality Project (SEWQ, 2005), Aquatic Ecosystem Health Monitoring Program (NRCMA, 2009), Clarence Valley Council (2009) and Eraring Energy (unpublished data 2005-2009). Ranges and medians were calculated for data points as near to sediment sampling sites as possible. Although the time span covered by individual datasets was variable most datasets covered multiple years. Sampling was predominantly monthly with sampling at 2 or more sites for periods ranging from 12 months to 14 years (1984-2010). Limited data was available for Pambula Lake (8 months).

Surface water quality data were collated and four different temperature terms were determined. The temperature terms calculated were water temperature at the time of sampling (Tsam), maximum summer temperature (Tmax), a 75th percentile temperature (T75) and 50th percentile (T50). Site latitude (Tlat) was also included as a potential proxy for temperature. These were chosen to provide a set of temperature values that encompassed a range of spatial and temporal (seasonal) temperature variabilities at each site that were then used for testing model sensitivity. Linear correlations between the temperature variables ($r^2>0.4$, $p<0.01$; n=40 Pearsons Critical Correlation Table) indicated that Tsam and Tlat were the only variables not significantly correlated or collinear to any other term. Thus, Tsam and Tlat were the only temperature-like variables used in further analyses. Despite almost all estuaries sampled possessing “restricted” entrances, estuary specific factors such as morphology and oceanic exchange are likely to contribute to the temperature regime (and other environmental variables) of each individual lake. Latitude itself may not be considered to be a proxy appropriate to represent gradients associated with temperature alone.

4.3.3 Laboratory techniques

Approximately 1-2 g of wet sample was weighed into 50 mL HDPE plastic vials and treated with a cold digestion of 20-25 mL of 10% hydrogen peroxide for 48-72 hours to remove organic matter. Samples were allowed to settle (3-5 days) and then the supernatant siphoned off, before adding 20-25 ml of high purity water (0.2 µm filter). A broken coverslip and 5-10 drops of 5% glacial acetic acid to each vial were added to reduce silica dissolution of frustules and retard nuisance algal growth, respectively (Parsons, pers. comm.). Samples were gently mixed before pipetting 1-3 mL of suspended sediment onto cleaned 40 x 22 mm coverslips and left in a dust free environment for the water to evaporate. Coverslips were then permanently mounted on pre-labelled glass slides with Norland Optical Adhesive 61 (Norland Products Inc., USA) and cured with ambient ultra-violet light (2-4 days). Samples were examined under oil immersion at 1000x magnification using a Leica DM2500 compound microscope with differential interference contrast (lens 100/1.25 oil) illumination. The microscope was equipped with a tri-focal head and a 10 megapixel Leica DFC480 digital camera controlled by Leica IM Version 4.0 digital imaging software (Leica Microsystems, Germany). A total of ~400 individual diatom frustules were identified to species level, where possible, according to recent scientific taxonomic literature. Taxonomy was predominantly based on Australian references (John, 1983; Saunders et al., 2010) and datasets (Taffs, unpub; Saunders, unpub) with reference to cosmopolitan floras (Witkowski et al., 2000). When fragmented valves were observed only specimens where greater than half the frustule remained intact were counted in order to not count the same specimen twice.

4.3.4 Statistical Analyses

Initial analysis of the nTL dataset was conducted using Bray-Curtis nested two-way similarity-dissimilarity analysis (SIMPER) in PRIMER 6 (Plymouth Marine Laboratories, U.K.), multivariate analyses in CANOCO 4.5 (Ter Braak and Šmilauer, 2002), and palaeoecological analysis and reconstruction in C2 version 1.6.8 (Juggins 2010). Environmental variables were checked for skewness and then log transformed (standard deviation >7 for salinity, dissolved oxygen, turbidity, ammonia, silica), centred and standardised for inclusion in the multivariate analyses. A total of 444 taxa were identified across the sampling program. To reduce the effect of artificial weighting caused by the presence of a large number of rare (low relative abundance score) species, any taxa with occurrence of < 1% relative abundance (RA) in at least 1 sample or a summed RA of < 5% across the dataset, were eliminated and contributed no further to the analysis. This resulted in a total of 177 taxa retained for statistical analyses (eTL1).

A gradient of 3.4 for the nTL1 dataset indicated that relationships in the species data were unimodal based on Detrended Correspondence Analysis (DCA) with detrending by segments and down weighting of rare species on untransformed data. Data was then transformed log (x+1) before being imported to CANOCO in an attempt to stabilise variance in the dataset (Birks et al., 2001).

A reduction in the number of species, similar to the method described above, for the extended eTL1 dataset (i.e. uneven or non-nested) yielded 186 species for further analysis. A DCA gradient of 4.2 indicated that relationships in the species data were also unimodal. In order to conduct sensitivity testing of the multivariate analyses and model performance, additional versions of the dataset were also generated. The removal of species with <5 % RA in any one sample and <5 % RA across all samples, yielded a reduced total of 63 species for analysis and formed the eTL5 dataset. Lowering the taxonomic resolution resulted in a dataset containing 45 genera (eTLg dataset). Therefore, the six scenarios used in the sensitivity iterations included:-

i. 80 sites x 186 species (eTL1);
ii. 80 sites x 63 species (eTL5);
iii. 80 sites x 45 genera (eTLg);
iv. 40 sites x 177 species (nTL1);
v. 40 sites x 63 species (nTL5); and
vi. 40 sites x 45 genera (nTLg).

Initially, Principal Component Analysis (PCA) and Canonical Analysis (CA) on species or environment data were performed on each of the six datasets, followed by Canonical Correspondence Analysis (CCA) on combined species data and environmental variables. Computations were conducted using forward selection and Monte Carlo permutation tests (999 permutations on the full model). Variance partitioning was then applied to identify which environmental variables accounted for independent, statistically significant variations in the diatom data (Saunders, 2011). Detrended Canonical Correspondence Analysis (DCCA) was used to determine which environmental variables were suitable for transfer function development (Birks, 1998) based on ratios of the 1st unconstrained to 1st constrained axis (i.e. eigenvalues $\lambda_1/\lambda_2 > 0.5$, Kingston et al., 1992). Species diversity indices were calculated using PAST freeware package (Hammer et al., 2001).

Transfer functions were developed using C2 software (Juggins, 2010) using weighted averaging (WA) with inverse and classical deshrinking, with and without tolerance downweighting, and weighted averaging partial least squares (WAPLS). Tests in WAPLS were employed to determine which models led to the best performing transfer function using cross validation (bootstrapping). Transfer functions with the best correlation (r^2), best predicted correlation (r^2_p), lowest root mean square error (RMSE) and root mean square error of prediction (RMSEP) were determined (Table 4.5). Details on the collection and analysis of a sediment core in Wyee Bay and the development of an earlier diatom-temperature inference model (Central Coast dataset) is provided in Chapter 2.

4.4 Results

4.4.1 Environmental variables and benthic diatom assemblages

Environmental data and longer-term water quality monitoring summary data for each system are outlined in Tables 4.2 and 4.3. Temperatures (Tsam) varied seasonally while all other temperature parameters correlated significantly with latitude (Tlat). Using Tmax, calculated from monitoring data, Tlat represented a change of 0.88 °C in water temperature for every 1° of latitude for this section of coast. A PCA of environmental data for all sites (eTL) indicated a separation of sites into lake groupings with nitrogen (NO_x, NH_3) and silica distinguishing sites in Wooleweyah, Cooroibah, Tuggerah and Brisbane Water; and PO_4 in Cobaki and

Teranora. Salinity delineated sites in southern Lake Macquarie, Tsam for sites near power station discharges and depth/Tlat for sites in Pambula, Womboyn, Smiths and Wallis lakes.

CCA of species datasets (eTL; nTL) indicated that 17-24 % of the variability in species assemblages was explained by the first two principal axes (Table 4.4). Sites within lakes generally grouped together for both the nested dataset (nTL1) and extended datasets (eTL) (Figure 4.2 and 4.3). Intra-regional gradients were generally greatest for the northern lake group compared to all other regional groups for eTL datasets. By comparison intra-regional gradients were generally of a similar magnitude to each other for nTL scenarios. For the eTL datasets the greatest gradient was that separating the northern lakes Cobaki and Teranora (and possibly Cooroibah) as well as the Tuggerah Lakes (BUD, MUN, TUG) sites from all other sites and groups. For the nTL dataset it was only these northern systems that consistently plotted separately to all other groups and sites for the different scenario types. In eTL scenarios Crangan Bay sites were similar to other Lake Macquarie sites and most dissimilar to northern lake and Tuggerah system sites. In nTL scenarios Crangan Bay sites were most similar to sites within the southern or mid-coast regions of NSW and most dissimilar to north coast and central coast sites.

For species-based scenarios (TL1, TL5) separation in the dataset was driven by relative abundances of key species including *Amphora australiensis* John, *Tryblionella granulata* (Grunow) Mann and *Navicula pusila* Smith for Cobaki and Teranora lakes (Figure 4.4a,d). The separation of Tuggerah Lakes sites in eTL scenarios was driven by the relative abundances of the pelagic species *Chaetocerous* sp4 and *Thalassiosira lacustris* (Grunow) Hasle as well as epibenthic *Cocconeis placentula var. euglypta* (Ehr.) Grunow (Figure 4.4a,b,c). Examination of the species datasets suggests that for the southern lakes assemblages were dominated by species including *Cocconeis* spp., *Licmophora debilis* (Kütz.) Grun. in Van Heurck and *Fallacia* sp. On the mid-north coast the benthic flora was dominated by the relative abundances of species including *Mastogloia pseudoexigua* Cholnoky, *Mastogloia fimbriata*(Brightwell) Grunow, *Synedra formosa* Hantzsch and *Cocconeis stauroneiformis* (Smith) Okuno.

Table 4.2 Sample site hydrochemistry data (this study).

Code	Depth m	Tlat °S	Tsam °C	Salinity	O_2 %sat	pH	Turbidity	NH3 $\mu g\ L^{-1}$	PO4 $\mu g\ L^{-1}$	NOx $\mu g\ L^{-1}$	SiO4 $\mu g\ L^{-1}$
CBH1	0.8	26.347	22.9	24.3	98.1	8.64	10.2	11.6	0.7	6.3	625
CBH2	0.4	26.348	21.9	18.6	94.9	8.48	10.0	14.5	0.3	7.1	893
CBH3	0.8	26.347	23.0	23.8	100.3	8.63	17.0	11.4	0.6	5.8	640
COB1	0.9	28.175	26.9	31.9	104.7	7.57	8.1	4.0	11.0	4.0	800
COB2	0.8	28.174	26.1	32.6	105.4	7.75	6.4	30.0	12.0	4.0	850
COB3	0.7	28.173	27.0	32.6	107.5	7.70	8.2	29.0	12.0	4.0	832
TEN1	2.8	28.206	23.6	34.1	105.6	7.84	13.1	4.0	12.0	4.0	760
TEN2	1.1	28.217	24.7	33.2	104.7	7.78	12.1	4.0	11.0	4.0	785
TEN3	1.1	28.222	26.1	32.1	103.6	7.75	16.4	4.0	13.0	4.0	790
WLW1	1.0	29.484	17.0	31.8	90.6	8.60	34.0	11.3	2.1	4.1	1113
WLW2	1.0	29.479	16.5	31.7	90.5	8.62	13.1	15.9	2.8	5.7	1039
WLW3	1.5	29.473	17.0	31.4	90.1	8.59	6.6	16.2	3.1	5.9	947
QNL1	1.2	31.621	21.2	30.4	79.6	8.62	1.1	4.0	0.1	1.1	550
QNL2	1.2	31.620	21.3	31.9	84.8	8.66	9.4	4.1	0.3	1.8	428
QNL3	1.2	31.619	20.8	30.8	98.0	8.81	9.3	5.2	0.3	1.4	450
QNL4	1.2	31.619	20.9	30.8	98.8	8.82	13.0	4.7	0.6	1.4	397
WAL1	3.5	32.264	20.7	32.7	100.8	8.18	5.0	5.5	0.8	0.7	448
WAL2	3.0	32.277	21.2	31.9	101.9	8.19	7.2	5.0	0.7	0.6	410
WAL3	3.0	32.306	20.6	33.0	95.5	8.18	3.7	4.5	0.9	0.7	446
SMT1	3.5	32.392	21.1	34.0	104.9	8.25	2.5	4.4	0.1	0.8	16
SMT2	4.0	32.386	21.2	34.2	104.1	8.22	3.2	6.0	0.4	2.1	15
SMT3	3.5	32.465	20.9	34.2	104.7	8.22	2.5	4.4	0.5	0.8	14
LMN1	3.3	32.991	14.9	33.9	99.8	8.19	1.5	1.8	6.9	0.3	359
LMN2	3.2	33.002	15.1	34.1	100.8	8.20	0.1	5.3	8.7	0.5	349
LMN3	3.3	33.003	14.9	34.0	101.0	8.27	0.1	1.9	7.4	0.1	338
LMW1	5.0	33.068	16.0	34.4	100.1	8.23	0.1	2.8	7.1	0.5	352
LMW2	2.6	33.057	15.7	34.0	95.9	8.21	0.1	1.9	7.6	0.2	330
ERG1	3.0	33.069	21.2	34.7	120.3	8.13	6.0	15.6	9.0	3.5	410
LMW1S	3.2	33.101	26.8	37.1	82.9	8.01	7.1	1.2	5.5	0.3	545
LMW3S	3.0	33.103	26.7	37.1	99.6	8.04	9.3	1.2	5.9	0.3	543
LMW5S	3.0	33.103	26.3	37.1	98.2	8.05	5.0	2.0	5.7	0.6	547
WBA	2.0	33.154	31.6	37.4	97.9	8.11	4.8	17.4	7.4	2.5	531
WYB1	2.8	33.152	28.7	36.1	91.4	7.81	1.5	14.9	4.8	4.1	515
WYB2	3.7	33.150	26.9	36.1	91.3	7.86	1.4	5.2	3.9	2.7	532
WYB3	4.7	33.145	24.7	36.1	97.4	7.91	1.3	0.8	2.8	1.7	540
WYB4	5.5	33.140	22.9	36.0	112.6	7.90	4.2	1.4	5.0	1.6	546
WYB5	6.7	33.137	22.9	36.0	98.5	7.92	1.3	0.9	5.3	1.4	535
CVB1	2.7	33.169	22.8	36.0	94.8	7.92	2.8	1.6	2.9	1.5	520
CVB2	3.7	33.166	22.6	36.0	94.1	7.95	2.0	1.4	2.8	1.3	530
CVB3	4.9	33.158	22.5	36.2	89.2	7.94	1.7	1.0	2.5	1.3	510
CVB4	5.7	33.152	22.8	36.2	91.0	7.93	1.8	1.5	2.7	1.4	505

Code	Depth m	Tlat °S	Tsam °C	Salinity	Dis. O2 %sat	pH	Turbidity	NH3 µg L^{-1}	PO4 µg L^{-1}	NOx µg L^{-1}	SiO4 µg L^{-1}
CVB5	6.2	33.144	22.9	36.2	93.6	7.94	2.0	2.7	3.0	1.3	500
CRB1	3.4	33.159	27.1	36.1	91.7	8.31	2.6	2.1	3.3	1.4	347
CRB2	4.0	33.158	27.1	35.9	96.6	7.89	1.6	0.2	2.6	1.3	371
CRB3	4.2	33.157	27.3	36.1	91.2	8.31	3.0	0.5	3.6	1.3	328
CRB4	6.8	33.154	22.1	36.1	91.8	8.30	3.8	1.8	3.6	1.3	335
CRB5	7.2	33.150	24.3	36.0	105.7	7.87	0.7	0.7	2.4	1.4	325
CRB11b	3.2	33.157	27.1	37.0	94.4	8.17	2.1	1.1	6.0	1.0	325
CRB21b	2.1	33.160	27.7	37.0	99.5	8.19	2.0	1.6	4.7	0.7	371
CRB23b	3.0	33.160	27.7	37.0	96.8	8.19	3.4	2.4	5.2	1.9	340
MUN1	1.6	33.197	25.6	23.4	92.4	8.13	5.9	9.2	0.9	2.3	1076
MUN2	3.0	33.201	25.8	23.4	93.0	8.14	7.5	9.1	0.6	1.6	1065
MUN3	3.4	33.218	25.9	23.4	94.7	8.11	5.5	6.1	0.6	1.3	986
MUN4	2.6	33.228	26.1	23.3	90.2	8.10	7.7	25.3	1.0	2.3	930
BUD1	1.6	33.224	30.7	23.3	99.1	8.03	11.1	33.8	0.6	7.3	1102
BUD2	2.1	33.237	27.7	22.7	99.8	8.18	10.8	6.4	0.4	1.6	699
BUD3	2.5	33.243	27.8	23.0	103.3	8.20	7.9	5.9	0.8	1.4	920
Tug1	2.6	33.274	25.5	21.4	99.6	8.25	8.5	5.7	0.0	1.4	85
Tug2	3.0	33.311	25.3	21.7	97.4	8.29	5.6	6.5	0.1	1.7	25
Tug3	2.6	33.340	15.9	15.8	105.1	9.19	1.1	7.5	0.7	2.1	1109
Tug4	3.0	33.322	15.9	15.9	103.7	9.16	0.8	7.4	0.8	2.5	1147
Tug5	3.2	33.285	15.8	14.4	109.4	9.23	0.2	115.0	0.8	6.3	1179
KCB1	3.2	33.480	12.5	33.2	98.2	8.55	4.4	5.1	3.5	1.2	139
KCB2	2.8	33.481	12.1	33.2	97.7	8.54	5.3	4.2	2.9	1.3	136
KCB3	2.5	33.496	12.1	33.3	98.0	8.52	2.8	3.8	2.9	1.7	119
BRW1	4.5	33.467	17.1	27.0	96.8	9.17	0.1	6.6	1.4	2.0	581
BRW2	4.2	33.446	17.2	26.0	103.5	9.24	0.2	6.6	0.9	1.7	574
BRW3	4.1	33.443	17.2	26.7	100.1	9.19	0.6	5.3	2.0	1.4	528
WYW1	3.0	33.495	12.8	32.8	98.9	8.41	4.3	4.0	4.3	1.2	151
WYW2	3.2	33.488	12.1	33.0	99.0	8.57	2.7	3.4	5.7	1.0	135
WYW3	4.2	33.476	12.1	33.0	98.1	8.64	1.6	4.6	5.3	1.7	124
TUR1	3.5	36.038	21.0	34.0	96.6	8.45	1.6	3.6	12.4	1.6	2041
TUR2	2.5	36.034	21.0	34.2	95.7	8.45	1.5	2.4	12.6	0.2	2015
TUR3	2.0	36.040	21.0	34.1	98.2	8.45	2.7	2.2	12.7	0.5	2018
PAM1	4.0	36.972	22.0	36.0	97.1	8.45	0.1	1.6	4.8	0.1	27
PAM2	3.5	36.970	21.0	36.0	96.6	8.49	1.0	1.4	5.0	0.2	24
PAM3	3.5	36.975	21.0	35.9	97.3	8.47	0.4	1.4	4.5	0.2	49
WMB1	4.0	37.240	22.3	33.9	95.8	8.18	0.1	4.3	0.8	0.6	466
WMB2	5.5	37.247	22.0	34.3	94.5	8.38	4.6	2.5	0.6	0.4	474
WMB3	2.5	37.246	22.0	34.3	96.1	8.42	0.1	2.5	0.9	0.4	512

Table 4.3 Medians for long-term monitoring hydrochemistry data

No	Name	Site Codes	Temp. °C	Sal	Dis.O_2 %sat	pH	Turbidity ntu	NH_3-N $\mu g\ L^{-1}$	NO_x-N $\mu g\ L^{-1}$	PO_4-P $\mu g\ L^{-1}$	SiO_4 $\mu g\ L^{-1}$
1	Cooroibah[1]	CBH1, CBH2, CBH3	24.4	22.6	95.0	7.95	10	17.9	15.4	2.0	-
2	Cobaki[2]	COB1, COB2, COB3	22.3	29.6	80.8	7.80	8	25.5	-	16.0	-
3	Teranora[2]	TEN1, TEN2, TEN3	22.3	29.9	89.5	8.00	11	21.0	-	16.5	-
4	Wooleweyah[3]	WLW1, WLW2, WLW3	22.1	28.3	96.8	7.88	6	18	2	1.0	-
5	Queens[4]	QNL1, QNL2, QNL3, QNL4	21.0	27.6	91.4*	8.73	5	4.4*	1.4*	0.3*	439*
6	Wallis[4]	WAL1, WAL2, WAL3	20.5	32.3	104.3	9.18	2	3.8	0.9	0.5	266
7	Smiths[4]	SMT1, SMT2, SMT3	23.1	26.3	97.9	7.92	2	10.6	5.4	0.8	350
8	Macquarie[4]	*WYB1-5,WBA,CVB1-5,LMN1-3,LMW1-2, ERG1,LMW1S,3S,5S,CRB4-5,11B,21B,23B*	20.7	34.2	97.2	8.2	3	-	5.0	16.2	580#
	Crangan Bay	CRB1, CRB2, CRB3	20.8	34.1	98.0	8.30	3	0.5	1.3	3.3	495#
9	Munmorah	*MUN1, MUN2, MUN3, MUN4*									
10	Budgewoi	*BUD1, BUD2, BUD3*									
11	Tuggerah[5]	*TUG1-2*, TUG3-5	19.7	30.1	101.7	8.91	4	4.0	11.2	0.7	450
12	Brisbane Water[4]	BRW1,*2-3*;KCB1,*2-3*;WYW1,*2-3*	20.9	33.3	92.1	8.11	5	45.1	11.2	9.9	-
13	Tuross[4]	TUR1, TUR2, TUR3	22.30	30.7	102.6	8.02	7	2.0	1.0	2.0	-
14	Pambula[4]	PAM1, PAM2, PAM3	20.67	34.8	102.0	7.90	4	2.0	1.0	-	-
15	Wonboyn Lake[6]	WBN1, WBN2, WBN3	19.00	31.9	96.7	7.67	4	-	-	-	-

[1] SEWQ, 2005; [2] AEHMP, 2009; [3] Clarence Valley Council, 2009; [4] CERAT, 2010; [5] NSWOEH, 2011; [6] Bega Valley Shire Council, 2005. * limited data available – this study; # from Eyre, 2005

For datasets limited to genus level classifications (eTLg; nTLg), the genera explaining the greatest gradients in the data were similar regardless if 80 or 40 sites were used (Figure 4.4c and f). Both sites from Cobaki-Teranora and the Tuggerah lakes were responsible as the driver of the largest gradients in both datasets. The genera associated with each of the estuaries in these scenarios, however, were generally different to those indicated within the species-based datasets. On a lake by lake analysis of the datasets Cobaki and Teranora were represented by the genera *Coscinodiscus*, *Acnanthes* and *Auricula*, while Smiths and Pambula were dominated by species of the genera *Diatoma* and *Licmophora*. Tuggerah-Budgewoi-Munmorah was defined by *Thalassionema* and *Stephanopyxis* as well as pelagic genera *Cyclotella*, *Rhizoselenia* and *Chaetocerous*. By comparison, the cosmopolitan genera *Cocconeis*, *Grammatophora* and *Surirella* contributed were not associated with any single lake or region.

CCA of species and environmental variables indicated 17% of the species and 46% of the species combined and environment data was explained by the first two principal axes for the eTL1 dataset and 19 % and 37 % for the nTL1 dataset (Table 4.4). While a reduction in the number of species and taxonomic resolution improved these values, a reduction in the number of sites did not. For the 11 variables tested the three most significant (p< 0.01) variables for each scenario contributed between 49 % (40 x 177 dataset) and 66 % (80 x 63 dataset) of the sum of all canonical eigenvalues according to the CCA analyses. The relative proportion of the sum of all eigenvalues improved with 40 sites compared to 80 sites. Environmental variables Tlat, salinity and PO_4 were consistently the strongest variables, explaining most of the independent variation in the datasets. These were followed by NOx, depth and Tsam.

While NH_3, NOx, turbidity and Si caused a separation of sites for Tuggerah and far northern coast sites (Figures 4.2 and 4.3), Lake Macquarie sites appeared to follow gradients of Tsam and salinity. Tlat and depth were significant variables for assemblages in the far south coast estuaries for all scenarios. Removal of Tlat from the CCA indicated that nutrients (NOx and PO4) followed by Tsam, explained the greatest variability in the dataset. DCCA analyses indicated that Tlat followed by salinity and PO_4 were the most consistent highly ranking independent variables explaining variation within the dataset (Figure 4.5).

Table 4.4. CCA and partial ordination output for sensitivity testing using the six dataset scenarios and 10 environmental variables.

Scenario #	Name	#sites x #species/ *genera*	Σ λ	Σ λ Canon.	% var. 2 axes spp.	% var. 2 axes spp.+env	Three variables explaining greatest proportions of variation from partial ordination (λ) 1st	2nd	3rd
1	eTL1	80 x186	2.49	0.78	17	46	Tlat (0.18)	Sal (0.16)	Depth (0.15)
2	eTL5	80 x 63	1.91	0.62	21	54	Sal (0.17)	Tlat (0.15	PO_4 (0.09)
3	eTLg	80 x *45*	0.91	0.33	19	62	Sal (0.08)	PO_4 (0.07)	Depth (0.06)*
4	nTL1	40 x 177	2.98	1.52	19	37	Tlat (0.27)	NOx (0.25)	PO_4 (0.22)
5	nTL5	40 x 63	2.29	1.19	24	46	Tlat (0.23)	PO_4 (0.22)	NOx (0.20)
6	nTLg	40 x *45*	1.08	0.56	25	48	Sal (0.11)	Tsam (0.10)	PO_4 (0.10)

* indicates variables where ratio of 1st and 2nd axes in a DCCA is <0.5 and the variable is unsuitable for transfer function development (Kingston et al., 1992).

Ratios (eigenvalues for first constrained to first unconstrained axis) for these variables and Tsam were always > 0.5 (eigenvalue ratio axis 1 vs axis 2) (Kingston et al., 1992) indicating they were appropriate for use in model development (Birks, 1998).

For the genus-based datasets, sites and lakes grouped together in regional settings similar to that found for species based analyses. In a CCA, however, a change in the significance of environmental variables was observed with a decline in the sum of eigenvalues. While salinity was a significant variable for all eTL scenarios, it only became prominent for nTLg and when Tlat was not one of the three strongest variables.

Plots of CA scores for a dataset containing 80 sites and Wyee Bay Number 1 Core (WB1C) subsamples (Chapter 2) indicated that assemblages from Wallis Lake were most similar to core subsamples from 11-23 cm depth than any other lakes or sites sampled. Core samples from 0-4 cm plot nearest to those from Wyee Bay, Chain Valley Bay and other Lake Macquarie sites compared to sites from all other lakes sampled.

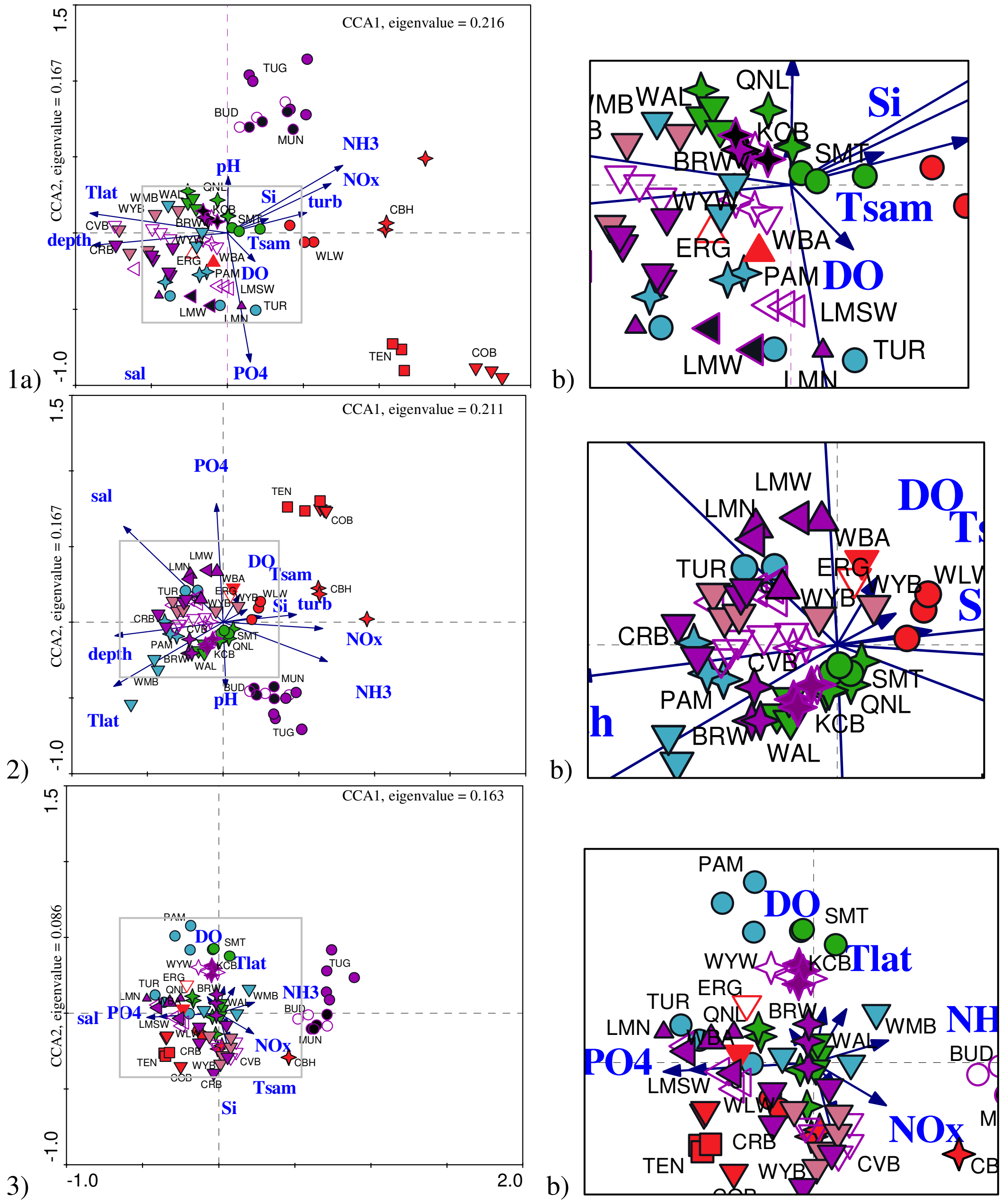


Figure 4.2. Biplots of principal component axes a) 1 & 2 and b) inset, from CCA analyses of 80 sites and 1) 186 species (eLT1), 2) 63 species (eLT5) and 3) 45 genera (eTLg). Symbols and colours denote lakes and groups north to south; CBH Cooroibah (♦), TEN Terranora (■), COB Cobaki (▼), WLW Wooleweyah (●), QNL Queens (♦), WAL Wallis (▼), SMT Smiths (●), LMN: LMW; LMS: LMSW Macquarie north, west, south, south-west (▲ ◀ ▼ ◁), CVB Chain Valley Bay (▽), WYB Wyee Bay (▲, ▼) & ERG Eraring (△), TUR Tuross (▼), PAM Pambula (♦) and WNB Wonboyn (●).

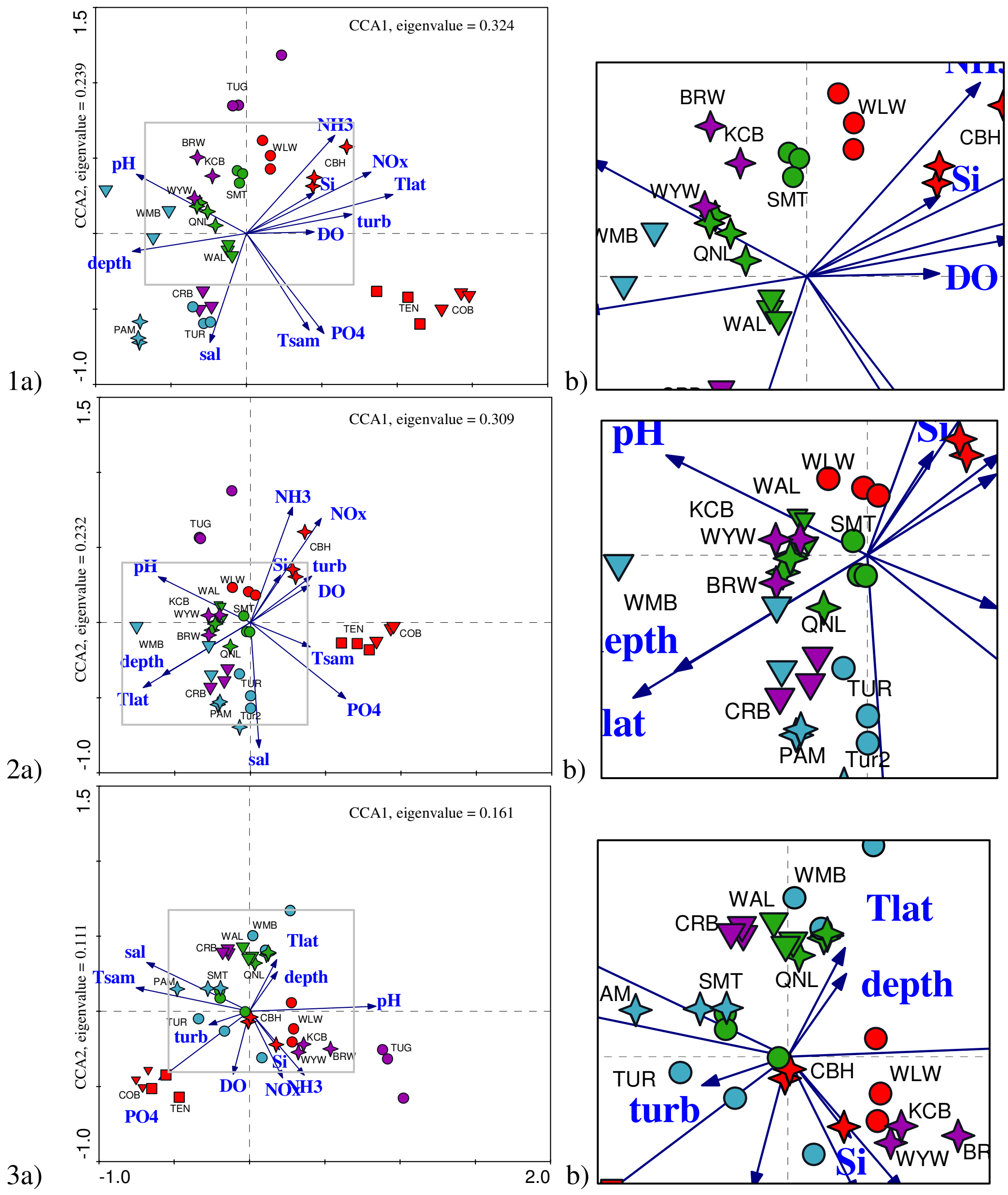


Figure 4.3 Biplots of principal component axes a) 1 & 2 and b) inset, from CCA analyses for 40 sites and 1) 177 species (nTL1), 2) 63 species (nTL5) and 3) 45 genera (nTLg). For a symbol and colour key see Figure 4.2.

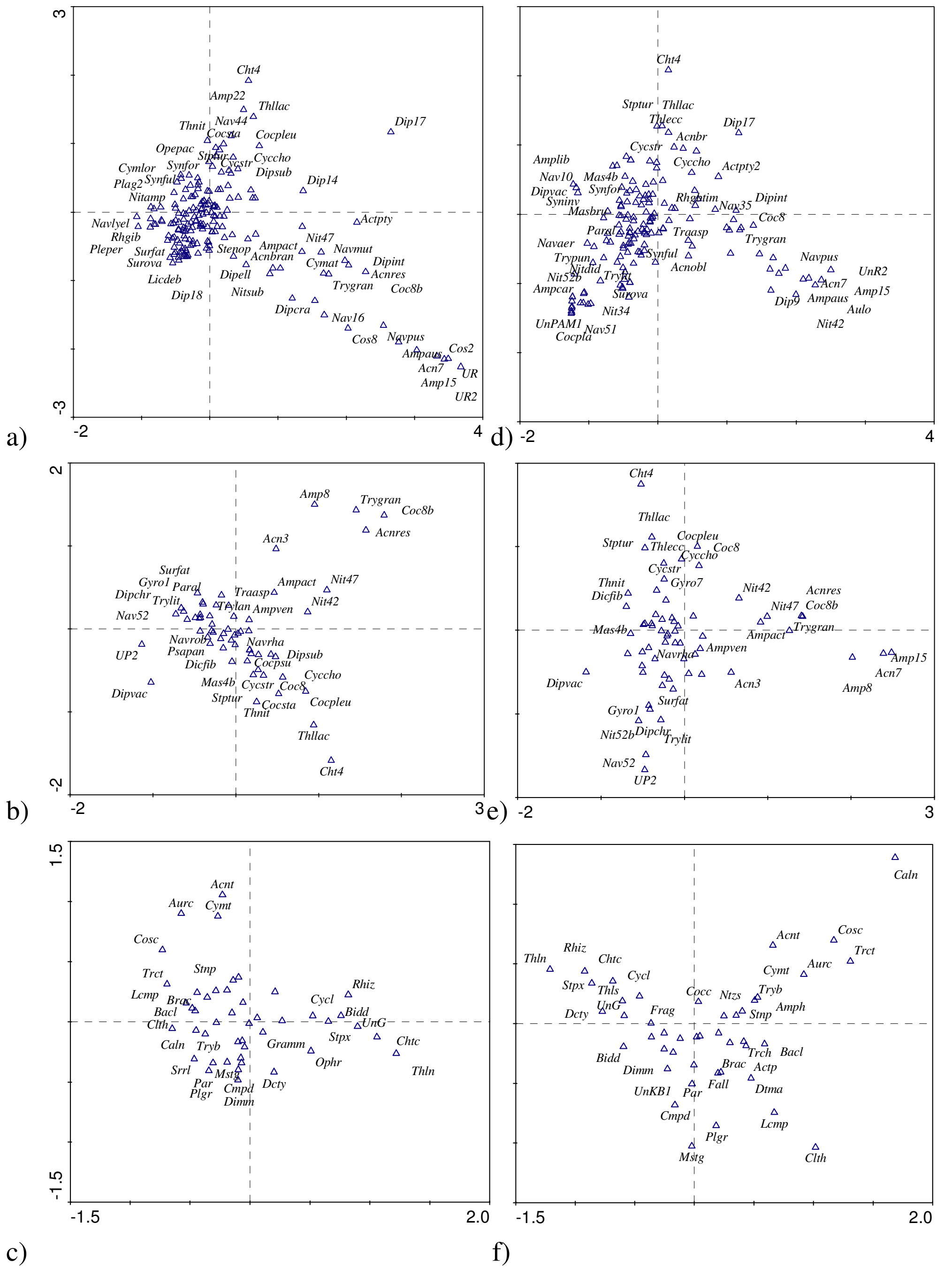


Figure 4.4 Scatter plots of principle component axes 1 and 2 from CCA analyses as species for each of six dataset scenarios, a) eTL1, b) eTL5, c) eTLg, d) nTL1, e) nTL5 and f) nTLg.

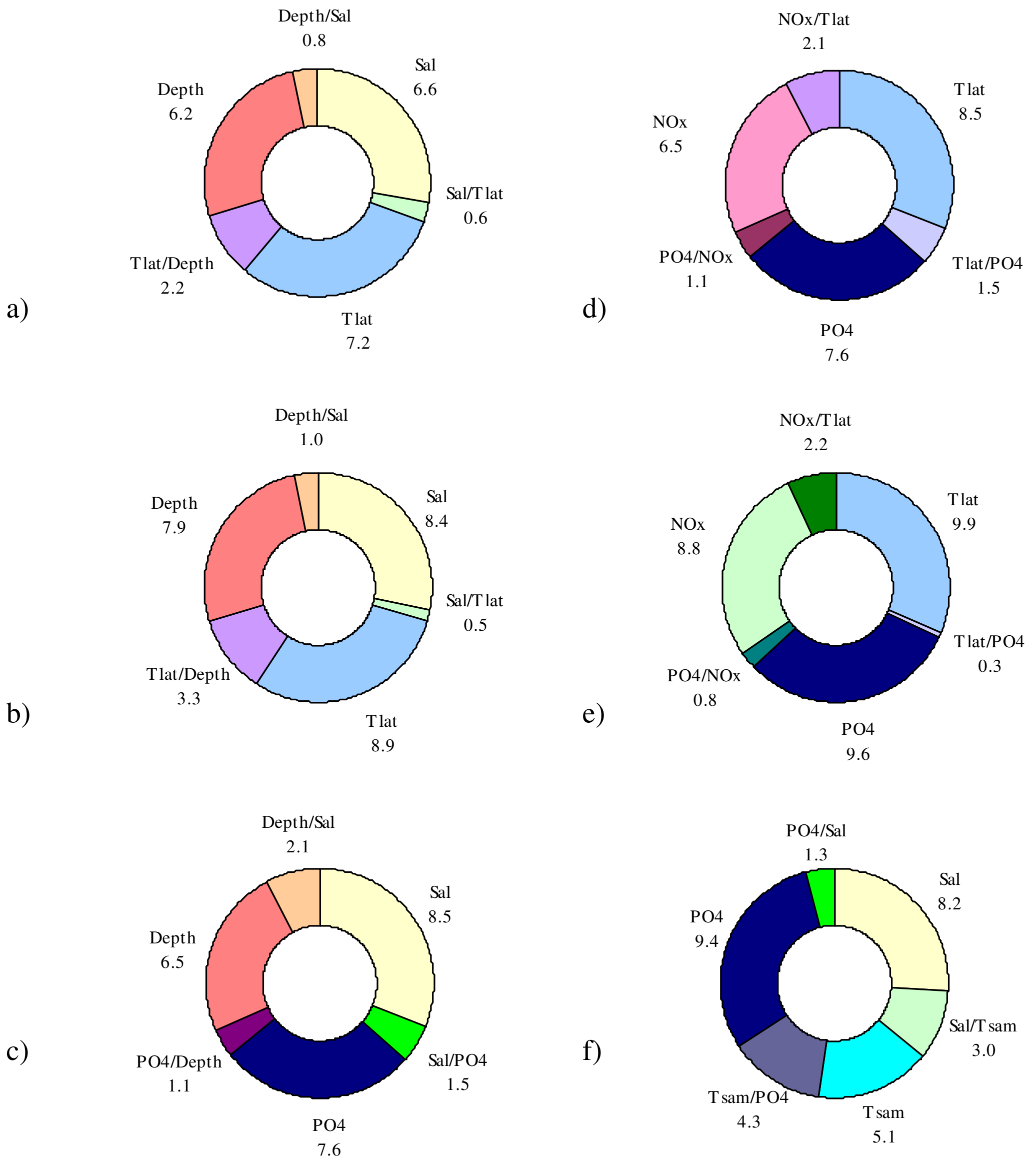


Figure 4.5 Doughnut charts denoting percent independent variation for each of the 3 most significant variables and relative 2-variables contribution from partial ordination analyses for the six dataset scenarios a) eLT1; b) eLT5; c) eLTg; d) nLT1; e) nLT5, and f) nLTg.

Table 4.5. WAPLS output of 6 scenarios for the three variables (11 available) with greatest r^2, r^2_p(boot) and lowest RMSEP and Tsam.

Scenario	Variable	WAPLS PC	Randomised t-test significance	r^2	r^2_p	RMSE	RMSEP	Units
80x186	Tlat	2	<0.005	0.94	0.86	0.25	0.39	°S
	PO_4	*3*	*<0.05*	*0.94*	*0.74*	*1.28*	*2.06*	*µg L^{-1}*
	Depth	2	<0.01	0.79	0.59	0.67	0.92	m
	Tsam	**2**	**<0.01**	**0.77**	**0.56**	**2.3**	**3.5**	**°C**
80x63	Tlat	2	<0.005	0.90	0.80	0.34	0.46	°S
	PO_4	3	<0.05	0.85	0.70	1.70	2.31	µg L^{-1}
	Depth	*2*	*<0.05*	*0.70*	*0.53*	*0.80*	*1.01*	*m*
	Tsam	**2**	**<0.005**	**0.69**	**0.56**	**2.62**	**3.48**	**°C**
80x45	*Tlat*	*2*	*<0.05*	*0.75*	*0.57*	*0.52*	*0.67*	*°S*
	PO_4	3	<0.05	0.85	0.65	1.40	2.19	µg L^{-1}
	Depth*	2	<0.01	0.70	0.53	0.81	1.02	m
	Tsam	**2**	**ns**	**0.90**	**0.69**	**1.16**	**2.45**	**°C**
40x177	Tlat	2	<0.05	0.97	0.89	0.23	0.48	°S
	PO_4	3	<0.05	0.99	0.89	0.45	1.55	µgL^{-1}
	NOx	2	<0.05	0.94	0.83	0.26	0.45	log µg L^{-1}
	Tsam	**3**	**<0.01**	**0.99**	**0.74**	**0.3**	**2.3**	**°C**
40x63	Tlat	2	<0.005	0.95	0.89	0.72	1.11	°S
	PO_4	2	<0.05	0.94	0.87	1.13	1.68	µg L^{-1}
	salinity	*2*	*<0.05*	*0.94*	*0.79*	*0.27*	*0.50*	*log*
	Tsam	**3**	**<0.005**	**0.97**	**0.75**	**0.64**	**2.33**	**°C**
40x45	PO_4	2	<0.01	0.86	0.71	1.69	2.46	µg L^{-1}
	salinity	3	<0.05	0.90	0.65	0.35	0.64	log
	Tsam	2	ns	0.90	0.69	1.16	2.45	°C

* indicates variables where ratio of 1st and 2nd axes in a DCCA is <0.5 and the variable is unsuitable for transfer function development. *Italicised text* indicates variables identified as suitable for transfer function development but not identified as one of the most significant variables according to CCA. **Bolded text** indicates where Tsam not one of three strongest variables according to individual variable CCAs when Tlat is included as an environmental variable in the dataset.

R^2_p (boot) and RMSEP of WA, WAPLS and PLS were compared for PC2 unless there was a >5% improvement with choosing additional principal components that was significant according to a t-test (Table 4.5). WAPLS generally performed equivalent to or better than PLS and both performed better than WA for all variables examined. The eLT1 and nLT1 scenarios had lower RMSEP values but generally similar r^2_p values compared to eLT5 and nLT5 scenarios, all significant to $p< 0.05$. Genera based scenarios generally underperformed relative to species based scenarios.

4.4.2 Species tolerances and ranges

Distributions of species across the ranges of latitude, salinity, phosphate and temperature from the eTL dataset are presented in Figure 4.6. Consistently higher species RA were observed between 31-34 °S for most of the 18 common species and is likely a reflection of the greatest concentration of sites around central coast lakes within the combined dataset. Despite this, some species appeared to be Tlat driven. For the species *Bacillaria paxillifer* (Müller) Hendey, high RAs were skewed to higher latitudes and for *Amphora acutiuscula* Kützing to lower latitudes. Species were predominantly marine-estuarine and of the salinity range 22-37. Some species, such as those of the genus *Cyclotella,* were present across the sampled salinity range of 14-37. *Cyclotella striata* (Kützing) Grunow and *Stephanopyxis turris* (Greville) Ralphs were skewed toward sites with low phosphate concentrations (< 3 µg L^{-1}) compared to *Bacillaria paxillifer* and *Surirella fatsuosa,* which were skewed to higher concentrations (5-15 µg L^{-1}). For temperature, all species RAs were generally greatest across the 20-27 °C range with a maximum of 32 °C for the dataset. Greater *Navicula rhaphoneis* (Ehrenberg) Cleve RAs were generally skewed towards sites with temperatures of 25-30 °C.

4.4.3 Temperature history reconstruction

Although Tsam was not often identified as one of the strongest variables, r^2 and r^2_p values were >0.56 and significant ($p< 0.05$). To determine if improvements in the temperature history reconstruction occurred as a result of the eTL and nTL scenarios compared to the earlier Central Coast model (Chapter 2), temperature values for 33 core depth slices (WB1C) using models from all six dataset scenarios (PC2 or 3) were reconstructed. Calculated temperature values were then plotted against a composite of air, lake water temperature and the ΔT anomaly values determined from long-term monitoring data (Chapter 2). Correlation coefficients (r^2) between predicted and monitored temperatures were calculated for each scenario (Figure 4.7). None of the correlations were significant at $p< 0.05$ (n=28, n-2 d.f.) according to a Pearson's Critical Correlation Coefficient Table. The nTL1 scenario, however, provided the greatest r^2 value of 0.33 (0.36 required to be significant).

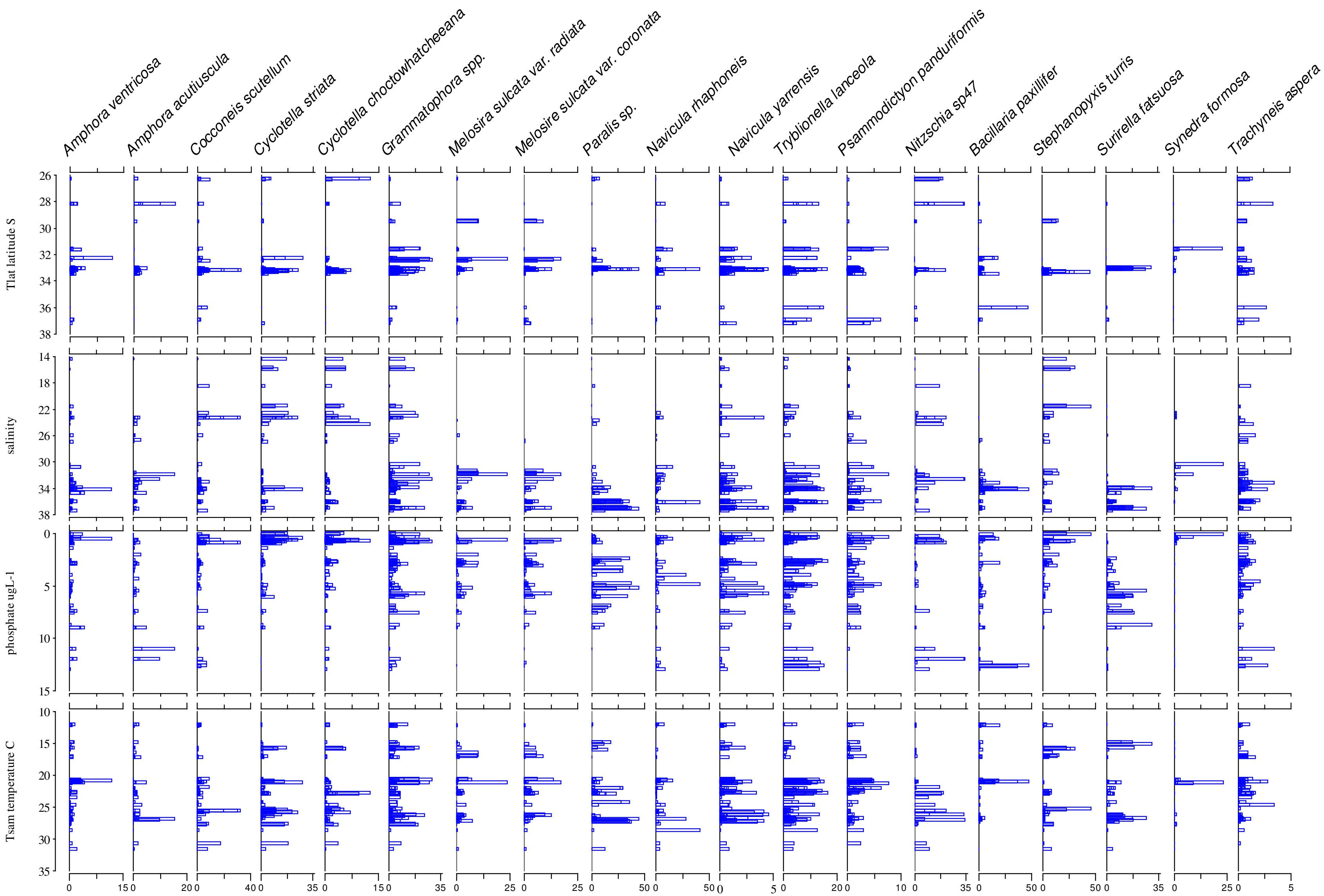


Figure 4.6. Tlat (ºS), salinity, PO_4 (µg L^{-1})and Tsam (°C) preferences for the 19 most common species of the eTL1 dataset.

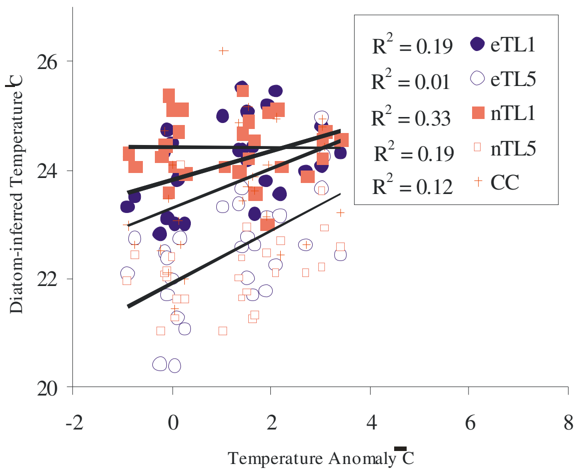


Figure 4.7. Correlations of diatom-inferred temperature from 4 species-based WAPLS scenario and Central Coast (CC) PLS models against ΔT (n=28).

Table 4.6. Mean reconstruction error values for Tlat and Tsam species scenario models.

Dataset Scenario **sites x species**	Name	Variable	Model PC	PC	Reconstruction standard error
80 x 186	eTL1	Tlat °S (equiv. 0.88 °C lat^{o-1})	WAPLS	2	± 0.20 °S
80 x 63	eTL5			2	± 0.26 °S
40 x 186	nTL1			2	± 0.31 °S
40 x 63	nTL5			2	± 0.42 °S
80 x 177	eTL1	Tsam °C	WAPLS	2	± 0.93 °C
80 x 63	eTL5			2	± 1.34 °C
40 x 177	nTL1			3	± 1.00 °C
40 x 63	nTL5			3	± 1.02 °C
51 x 141	Central Coast	Tsam °C	PLS	2	± 1.08 °C

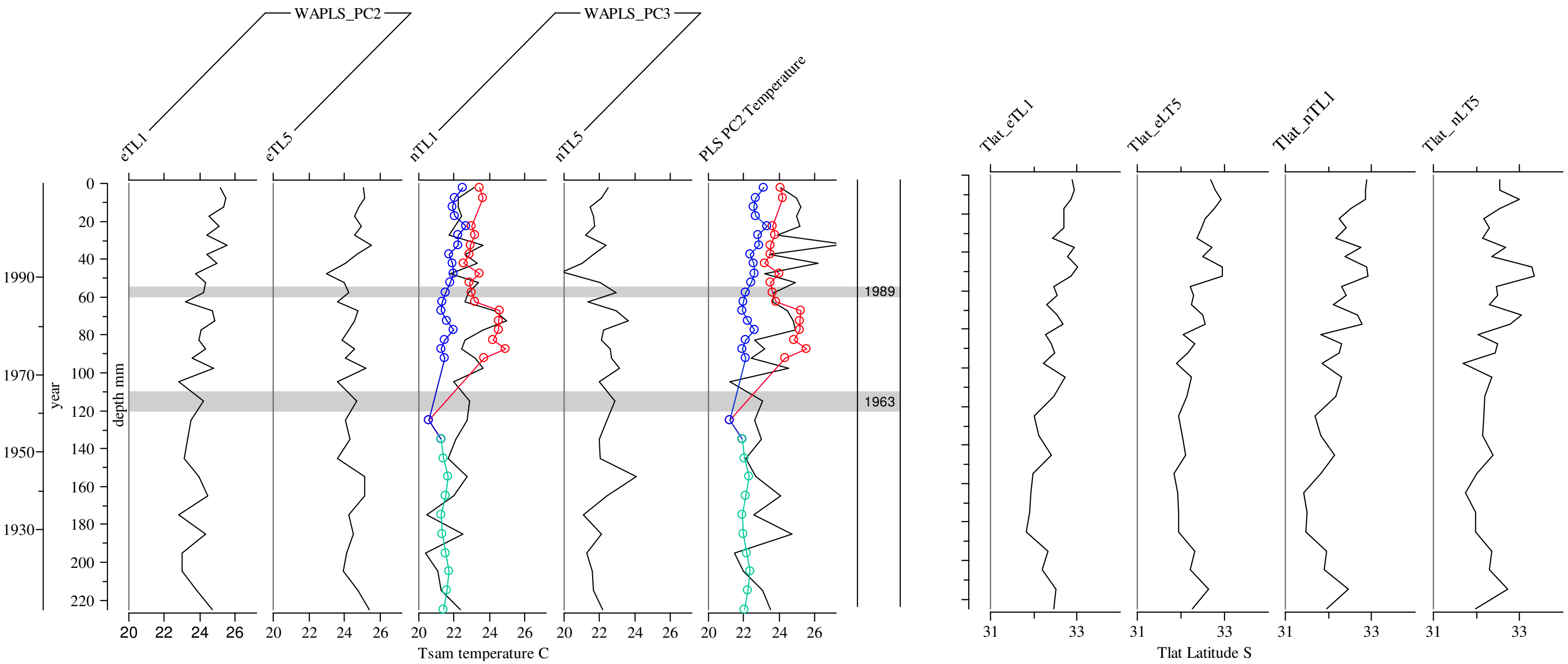


Figure 4.8 Diatom-inferred reconstructions for a) Tsam from WAPLS models from 4 dataset scenarios (this Chapter) and the Central Coast dataset PLS PC2 (Chapter 2), lake water temperature anomaly (blue), air temperature anomaly (green) and ΔT (red) from CSM values of field monitoring data scaled to an average pre-power station air temperature (21.5 C – nTL1; 22.13 – PLS PC2; b) Tlat from WAPLS PC2 models from 4 dataset scenarios.

Down core profiles of reconstructed temperature and monitoring data are presented in Figure 4.8 along with Tlat profiles. The Tsam model based on the nested nTL1 dataset appears to produce the best estimate of changes in water temperature in the Wyee Bay core compared to other models. Reconstructed Tlat describes a trend of increasing latitude (decrease in temperature) over time and towards the surface of the core. Conversely, water and air temperatures in Wyee Bay and Lake Macquarie had an increasing trend for 1910-2003.

Reconstructed temperature (Tsam) based on eTL1, nTL1 and nTL5 datasets improved reconstruction standard errors (rSE) values by between 6-14 % compared to rSE from the central coast model (±1.08 °C) (Table 4.6). rSE for Tlat scenarios were significantly better than those for Tsam reconstructions at < ±0.42 ° S latitude (equivalent to ~ ±0.48 °C $°lat^{-1}$) for all species-based scenarios. The rSE values for genus-based scenarios were 3-4 times greater than those determined for reconstruction using species datasets. Thus, genus-based reconstructions are not presented.

4.5 Discussion

4.5.1 Sensitivity of spatial patterns to dataset variability

From the datasets collected here, it is apparent that distributions of benthic diatoms in southeast Australian estuaries are dominated by a combination of environmental factors including latitude, salinity, nutrients (phosphate, oxidised nitrogen), temperature, depth and pH. While latitude is the most dominant variable, once removed salinity, temperature and nutrients dominate assemblage gradients for coastal lakes. Similarly, there is a decline in the prominence of Tlat when species datasets are reduced to the level of genus. Ultimately, if latitude were considered to not strictly be an "environmental" variable and removed, then at the very least the analyses highlight the importance of the sampling across the range of the variable of interest. This issue has been raised in relation to datasets developed to infer temperature specifically (Nichol, 2000; Bilger and Hall, 2003).

For south-east coast estuaries of NSW and southern Queensland, broad groupings of lakes and sites, and the environmental characteristics driving their separation from other lakes, were generally consistent regardless of the dataset used. Telford and Birks (2011) indicated that the size of the training (reference) dataset was less significant when reconstructions were based on localised reference datasets compared to ones developed across large geographic or environmental gradients. From sensitivity testing, greater numbers of sites (expanded dataset) and species provided for better performing models. In reconstruction, however, the structured dataset 'evenly' spread over the coast provided the temperature-inferred profile that predicted real-time temperature most closely.

According to the contemporaneous diatom data, while phosphate and nitrogen distinguished benthic assemblages in Teranora Broadwater and Cobaki Lagoon nitrogen was the significant driver of assemblages for the urbanised estuaries of the Tuggerah Lakes. The species *Cocconeis placentula* Ehrenberg dominated some sites in Tuggerah Lakes and has been identified as an indicator of environments with fluctuating salinities (Leterme et al., 2010). Salinity appeared to govern assemblage distribution for systems with restricted tidal flushing (Lake Macquarie, Tuross Lake) where factors such as evaporation and catchment inflows dominate (Roy et al., 2001). In relatively unmodified, pristine and/or well-flushed systems, such as Wonboyn, Pambula, Kincumber Bay, Wyong water, Wallis Lake and Smiths Lake, latitude and depth were dominant environmental variables. When reduced to 40 sites (nested dataset), however, these less modified systems were not associated with any individual environmental variable. Thus, even for relatively unmodified systems, concluding that a specific environmental variable as a definitive driver of a lake's assemblages should be treated with caution. Similar to AusRivAS and macroinvertebrates, however, a series of reference lakes/systems or conditions could be established and diatom assemblages further tested and developed as biomonitoring tools and estuarine condition indices.

Importantly, assemblages within the lakes' control embayment, were more similar to these less modified systems than the highly modified systems. This suggests that Crangan Bay may be considered to be in reasonable health relative to other systems and for the parameters investigated. Crangan Bay assemblages and some other Lake Macquarie sites were structured by salinity and not nutrients. Sewage discharges to the lake ceased around 1994 and nutrients were associated with relatively higher chlorophyll concentrations and incidences of algal blooms in the 1990s (AWACS, 1995). Thus, benthic diatoms support the evidence for reduced nutrient pressures on the lake in recent times. The species *Navicula arenaria* Donkin has been identified previously associated with unpolluted sites on the NSW north coast (Logan et al., 2010) and was found in less modified bays of modified to highly modified Crangan Bay and Kincumber Bay as well as relatively unmodified systems as Cooroibah and Wonboyn.

4.5.2 Temperature Transfer Function

Development of a benthic diatom dataset across a latitudinal gradient for reconstruction of a temperature history for Wyee Bay improved model performance with a 7% decline in rSE values when using the nTL1 compared to a localised (Central Coast) dataset. Reconstructions based on this larger and geographically broader dataset, however, were not significantly correlated with data obtained from monitoring programs (Chapter 2). Due to length of the core and limited number of sample depths (n=33) the dataset was inadequate to achieve a significant correlation. Longer and/or greater resolution core intervals may yield a greater number of samples for a correlation. Other factors associated with variability in sedimentation rates, ^{210}Pb dates and or calculation of the CSm values, however, may also provide additional slice-by-slice uncertainty when comparing modelled and monitored data values. Broad relative temperature changes between pre-power station, 1963-1989 and 1989-2003 periods, however, can be distinguished and align with general operational changes at the power station (Chapter 2). Generally, the nested dataset provides an improved 'best estimate' of a water temperature history for receiving embayment of Wyee Bay during the period 1910-2003. The pre-power station temperature of ~21.5 ºC shifted towards 25 °C during 1963-1989. This has since reverted to 23 °C under the current power station operational regime.

While Tlat possessed lower standard errors (best was eLT1) of reconstruction and provided a potentially more robust and quantitative alternative temperature proxy, the Tlat model described an increasing latitude (cooling trend) at the Wyee Bay site since 1910. Long-term temperature data, however, indicated a temperature increase for the period (Chapter 2) and this is in-line with other regional climatic assessments (Cai et al., 2005; Lough, 2007; Thompson et al., 2009).

This raises the question: can latitude be considered to be independent of temperature? Certainly, the temperature-latitude relationship is likely to be inherently more complex. Lakes of similar latitudes can differ geomorphologically depending on their stage of evolution each possessing a distinct hydrology driving salinity, temperature and other water quality variables (Roy et al., 2001). For temperature, this is supported by the long-term monitoring data where annual median temperature for lakes of similar latitudes varied by ~2 °C (Table 4.2). Additionally, geographical factors including light, solar radiation, seasonality and geology may also have contributed more significantly to assemblage gradients than temperature.

If latitude was a proxy for temperature then assemblages in the "warming" waters of Wyee Bay and preserved in the sediments would have been expected to increasingly be represented by species from lower latitudes (warmer) over time. However, this is not the case. The relationship between latitude and temperature, in this case, is confounded by an assumption of the palaeoecological technique that infers contemporary environmental conditions based on modern assemblages on to a fossil assemblage dataset. If benthic diatom assemblages at any given location have changed as a result of range extension of species and changing climate, then use of assemblages from a single temporally limited period as a reference are invalid.

With increasing water temperatures associated with the strengthening of the EAC, then, similar to other species, benthic diatom assemblages are likely to be advancing south with changing climate. A sample collected in Wonboyn today would possess an assemblage, that 100 years ago (on a linear scale) was living further north (1-2 °lat) near Jervis Bay. Thus, a sample of fossil diatoms from 100 years ago within the core would be wrongly attributed to sites of lower relative latitude than that when they were deposited. This may be one mechanism to explain the trend of decreasing latitude with depth in the WAPLS Tlat model. For range expansion itself, however, changes in diatom species along the coast with time are unlikely to have been linear and mechanisms for translation of pioneering species into estuaries would have been variable. Anthropogenic factors will have also have contributed to diatom distributions in modified systems. Lake specific factors such as lake morphology (hydrology, tidal prism), level of anthropogenic modification and the small sample size (n=13) might have all contributed to a level of stochastic variability around a term of "latitude". For this reason, "latitude" cannot be considered an adequate proxy for any single environmental variable including temperature.

Philibert et al. (2006) suggested the development of reference datasets across small geographical ranges to reduce the influence of location potentially obscuring the variance explained by other measured water quality variables. A small range, however, would not have achieved an adequately sampled natural temperature gradient. Although latitude is not a good proxy for temperature, the temperature gradient sampled covered the range of elevated temperatures for the Wyee Bay site (Chapter 2) and then used for the development of the temperature transfer function. When Tlat was removed from scenarios, Tsam, salinity and nutrients were the most significant variables in the datasets. Issues with temperature-transfer functions have been reported for Swedish lakes (Bilger and Hall, 2003) where pH was determined to be an over-riding factor masking a temperature signal. Anderson (2000) indicated that temperature functions should be treated with caution, except when they represent changes over large climatic scales or are associated with anthropogenically induced gradients.

4.5.3 Further considerations and Implications for Management and Monitoring

As discussed in Chapters 1 and 2 the WB1C core was obtained from an area of the thermal plume exposed to ΔT values generally <3 °C. Reconstruction errors remained high (± 1.0 °C) and the temperature model was unable to accurately predict temperature changes over small temporal scales. Over greater time scales, however, the direction and magnitude of change was determined and delineated three distinct periods within the temperature reconstruction. An increase in mean water temperature of 2-4 °C was observed from pre- to post-power station commissioning followed by a reduction in Wyee Bay temperatures around 1989. Pre-power station diatom-inferred water temperatures were ~22-24 °C according to previous models (Chapter 2) compared to 21-22 °C for the nTL1 model. This new temperature transfer function provided a more accurate representation of the temperature history for Wyee Bay across the period of power station operation and a more reliable estimate for lake temperature baseline conditions.

Obtaining an "adequate" reference dataset is complex as the dataset must achieve adequate site representation and replication over the environmental gradient of interest (Anderson, 2000). It also must be restricted in its geographical range (Philibert et al., 2006), whilst avoiding autocorrelation (Telford and Birks, 2009). The temperature-model based upon the natural temperature gradient and encompassed in sites of the nested dataset (nTL), excluded data from sites lying within the artificial temperature gradient of power station plumes. The data, therefore, can be considered to be mutually exclusive and not suffer from issues associated with autocorrelation (Telford and Birks, 2009). The technique assumes that species in an environment with artificially elevated temperatures are responding in the same manner as if they were exposed to a natural thermal gradient. The latitudinal gradient sampled was adequate (7-8 °C) to cover an equivalent maximum ~3 °C ΔT observed at the WB1C core site.

A qualitative examination of the temperature ranges and species RAs (nTL dataset – no plume affected sites) across the dominant species in the dataset suggests those species that appeared to be most responsive to the natural temperature gradient were the same species that responded to the artificial gradient (Chapter 2). Two species *Navicula rhaphoneis* and *Tryblionella lanceola* identified as key indicators of the plume in Chapter 2 are also skewed toward sites with higher water temperatures within the natural temperature gradient. The same trend was also observed for the eTL dataset for these species with water temperature optima in the range 23-28 °C. A thorough quantitative analysis with the calculation of species optima and tolerances (Huismann-Olff-Fresco models) would need to be conducted to fully test this relationship.

The dataset established here is the first of its kind providing a broad spatial database of contemporaneous benthic diatom assemblages, species and environmental variables for estuaries of the southeast coast of Australia. The study builds on other recent broad scale surveys of benthic diatoms in estuaries and the development of salinity-transfer functions for Tasmania and Victoria (Saunders, 2011) and northern NSW (Logan and Taffs, unpub.). For NSW, the ranges of benthic diatoms and taxonomical descriptions of species were published in the 1950-1960s from surveys of estuaries and major ports of south-east Australia (Crosby and Ferguson Wood, 1959; 1960). Although, broad generalised groupings of species distribution (marine, estuarine, brackish) were provided, details of tolerances and optima of species relative to key environmental variables were lacking.

The database of species distributions and environmental variables for Noosa to Eden might be combined with other south-east datasets for the development of indices for system health assessment similar to that for AusRivAS (Turak et al., 1999). Macroinvertebrates are monitored across Victoria, NSW and Queensland systems using family level identification and environmental data to indicate river system health. For the purposes of applying diatoms as a monitoring tool for estuaries, genera level taxonomic data has demonstrated to be of adequate resolution to broadly distinguish lakes relative to pristine systems. A total of ~37 benthic diatom families were identified in the current eTL1 dataset. As to whether a lower taxonomic resolution such as family yields similar results to that of genera or species-based datasets, is yet to be examined.

4.6 Conclusions

Although reductions in taxonomic resolution may be adequate to delineate lakes and describe general trends relative to the main environmental variables, genera level datasets produced poorer performing transfer functions compared to species level datasets. Those relationships between environmental variables and systems, however, were generally consistent across dataset types with benthic diatoms being suitable for development of indices for broadscale-type system health assessments.

While temperature was masked by other stronger variables when latitude was included within environmental datasets, it was consistently one of the strongest and most independent variables when latitude was removed from the environmental datasets. Temperature transfer functions and reconstruction standard errors improved in comparison to functions and errors for previous localised datasets. A relatively even and nested dataset provided a reconstruction that was most significant when validated with long-term water temperature proxies. For this study, the diatom-inferred temperature indicated that temperature regimes within the receiving water bay varied over different power station operational periods. Water temperatures at the core site in Wyee Bay were several degrees cooler during pre-power station times compared to temperature under the current power station operating regime.

Species responding to anthropogenically induced temperature gradients are the same as those responding to natural ones. Thus, those species observed at sites of greater temperatures within thermal plumes are likely to provide an indicator species for use in predicting changes with further temperature increases and range extension along the coast for estuaries of the region.

5. Event Horizons

Benthic diatoms, heavy metals, ^{210}Pb and ^{7}Be as multiple markers for validating sediment chronology and inferring past lake water quality for southern Lake Macquarie.

Abstract

Historic contamination of sediments in the north of Lake Macquarie with heavy metals such as Cd, Cu, Pb and Zn has resulted in lake-wide enrichment of sediments that is a continuing legacy for the lake and its ecological systems. To investigate potential differences in the sedimented diatom assemblages at control and impact locations prior to the onset of anthropogenic contamination and thermal discharges two sediment cores were obtained from southern Lake Macquarie. Cores were obtained from a site within 500m of the discharge of thermal plume in Wyee Bay (WBA) as well as from a historic lake control location in Crangan Bay (CBA) and analysed for heavy metals, ^{210}Pb, ^{7}Be and diatoms. While the ^{210}Pb profile of the Wyee Bay core was considered to be too disturbed for metal history and palaeoecological analyses, the Crangan Bay core was intact with a chronology and metal profile analogous to that of previous studies. Only comparisons between assemblages within the CBA core and an earlier core from Wyee Bay could be achieved. From a history of key sources, combined with previous sediment metal studies, it was apparent that Cd and Zn contamination first occurred in northern Lake Macquarie in the mid-1920s and was redistributed as far south as Crangan Bay within 5-10 years. For the less mobile metal Cu, redistribution to southern Crangan Bay appeared to either be occurring over a much greater time scale (30+ years) or, more likely, derived from more recent diffuse sources. Diatom assemblages of pre-metal contamination sediments from the Crangan Bay core were most similar to ~pre-1935 assemblages from the Wyee Bay core (WBC1), pre-dating commissioning of the Vales Point power station (1963). This indicates that, prior to 1935, Crangan Bay and Wyee Bay experienced similar environmental conditions and may represent the “status” of the pre-anthropogenic (power station and metal contamination) lake leading up to this time. The data provides an indication of water quality within southern Lake Macquarie prior to power station commissioning over a period when data was limited and/or completely absent.

5.1 Introduction

For Australia, arguably the greatest anthropogenic change to coastal environments during the Holocene began with European settlement ~220 years ago. Continued rural, urban and industrial development associated with population growth occurred along the east coast and has contributed to increased pressure on estuarine systems. For the organisms that live or have lived in these estuaries, the numerous and varied human induced pressures add to an already complex relationship between organisms and their environment that govern their abundance and distribution. Because of this complexity, multi proxy studies are the preferred approach to understanding ecosystem function and health and the effects of multiple stressors on systems (Niemi et al, 2004).

Heavy metal pollution is one pressure that can affect distributions of organisms in estuaries (Simpson et al, 2005) and have implications long after the initial pollution source has been removed. To establish natural from unnatural metal levels, cored sediment profiles and dating can be used to reconstruct contaminant histories and determine background concentrations (Olmos and Birch, 2010). In isolation, however, the data do not allow us to understand pre-industrial system health. Methods that reconstruct past environments, such as palaeoecology, are powerful techniques and can be used for inferring past system status and establishing reference conditions (Dixit et al., 1992).

Estuaries in particular are ideal candidates for palaeoecological studies as many of them contain well-preserved records of environmental variability that span the last 10,000 years (Nichol, 2001). A diverse range of palaeoecological techniques and proxies have been applied to aquatic systems across south-eastern Australia. These have included the use of fossil pollen (McMinn, 1992), crustacean tests (Ralph et al., 2011), diatoms (Tibby et al., 2003; Saunders et al., 2008; Logan et al., 2011), pigments (Hodgson et al., 1998) and dinoflagellate cysts (McMinn et al, 2003) to examine historical changes in ecology, water quality and climate.

The effects of anthropogenic pollutants from point source discharges on estuarine systems of south-eastern Australia and the adjacent coastal marine environment have been studied extensively (Chapman et al, 1995; Roberts et al., 1998; Birch and Taylor, 1999). Heavy metals and pesticides delivered to waterways from past industrial practices and urban runoff have, for example, resulted in high metal loads to many NSW estuaries (Birch et al, 1997; Birch, 2000) that pose a risk to system ecology (Simpson et al, 2005). In the estuarine environment contaminants bind to sediment particles and are either transported by water currents or in low energy environments settle to the lake bed where they become incorporated into bottom sediments. Once buried and under reducing conditions many metals become relatively immobile (Peters et al, 1999b) and, provided they remain undisturbed, these sediments can be cored and the metals analysed to retrieve a record of the pollution history at a site (Kilby and Batley 1993).

Radioactive isotopes of some metals, derived from erosion of catchments and/or processes in the atmosphere, are also delivered to estuaries and become preserved within sediments. This radioactivity together with its predictable rate of decay is used widely (Ritchie and Ritchie, 1995) to date lake sediment stratigraphy (Zapata, 2002) and provide indicators of core chronological robustness (Heijnis, pers. comm.). Suitable radioisotopes with half lives appropriate for dating Holocene sediments range in time scales from days (Berrylium-7 (^{7}Be) – half life 53 days) to thousands of years (Carbon-14 (^{14}C) – half life 5730 years). Others, such as Caesium-137 (^{137}Cs – half life 30 years) derived from fallout associated with the commencement of atomic testing in 1954, are used to pinpoint key event horizons, Lead-210 (^{210}Pb – half life 22.3 years), however, is the principal isotope available for determining the age of lake sediments at inter-annual time resolution over timescales of 100-150 years (Zapata, 2002). The method has been used widely to provide chronologies and examine environmental change in southeast Australian estuaries over modern timescales from the Hawkesbury River (McMinn et al., 2003), the Gippsland Lakes (Reid 1997; Saunders et al., 2008) and Tasmania (McMinn et al., 1997; Saunders et al., 2007). While palaeoecological techniques are applied as a powerful tool in the management of ecosystems in the USA, their broadscale application to Australian estuarine ecosystems is yet to be realised (Saunders and Taffs, 2009).

The aim of this chapter was to determine heavy metal and ^{210}Pb profiles for sediment cores from plume effected (Wyee Bay) and a control embayment (Crangan Bay). Metal and radio-isotope data were used to determine and cross-validate a sediment chronology and pinpoint the pre-industrial (pre-metal contaminant) horizon within the sediments. These deeper core layers were targeted for fossil benthic diatoms analysis and then test null hypothesis that benthic diatoms of the pre-industrial era were not significantly different between plume affected and control locations. Assemblages were also used in the attempt to delineate pre-power station and pre-metal contaminant periods and infer past lake conditions.

5.1.2 Location and Background

The estuary of Lake Macquarie has been exposed to varied pollution pressures over the past 200 years. These include urban and rural development, sewage discharges, colliery wash plants, a metal foundry, power station stack emissions, ash dams and effluent from a chemical plant and smelter (Kilby and Batley 1993). The operation of the Pb-Zn smelter (1897-2003) and delivery of wastes to Cockle Bay was the greatest single source of heavy metal contamination to the lake since European settlement (Roy and Crawford, 1984; AWACS, 1995). Despite significant improvements to environmental regulation and management practices in the 1970s, in 1981 ~1 tonne of Pb, Zn and Se and 0.5 tonne of Cd was being discharged from the smelter to Cockle Creek (SPCC, 1983). In combination with other sources, sediments of Cockle Creek, have contributed to widespread metal contamination of lake sediments. Although metal concentrations are in decline (Roach, 2005) historic metal contamination continues to affect lake ecology (Roberts, 1999: Peters et al., 1999a; Simpson et al, 2005).

The lake is a natural mud basin and provides relatively continuous record of Holocene deposition within its sediments (Roy and Crawford 1984). While studies have focused on the effects of metals on specific organisms (Batley, 1987; Robinson 1987; Roberts, 1999; Kirby et al., 2001; Simpson et al., 2005; Roach et al., 2008) a smaller number of studies have examined spatial and temporal distributions of metals in sediments (Roy and Crawford 1984, Batley 1987; Olmos and Birch 2010). For these geochemically-based investigations, the identification of background, or pre-industrial concentrations, has been achieved by establishing geochemical profiles and identifying subsurface minima (Kilby and Batley 1993; Peters et al., 1999a; Roach 2005).

The use of isotopes to date sediments, estimate depth ages and calculate sedimentation or mass accumulation rates, by comparison, has generally been less common. While Roy and

Crawford (1984) dated fossil shell material using ^{14}C and calculated sedimentation rates of ~0.15-0.5 mm year^{-1}, more recent work using ^{210}Pb determined rates of 1.1-5.5 mm year^{-1} near Cockle Creek (Kilby and Batley 1993). Sedimentation rates in the northern lake at Cockle Bay are bimodal with 4 mm year^{-1} for 1897-1952 and 14 mm year^{-1} for 1953-2003 (Olmos and Birch, 2010). These rates overlap with but are toward the higher end of rates reported for Nords Wharf in the southern lake at 1.5 mm year^{-1} 1921-1987 and 5.7 mm year^{-1} 1981-1999 (Peters et al, 1999b). A heavy metal profile of a core (~108 cm) collected in 2003 at the southern end of Crangan Bay identified enrichment of copper (Cu), cadmium (Cd), lead (Pb) and zinc (Z)n in the upper 20 cm but provided no dating validation (Olmos and Birch, 2010). The use of metal profiles, ^{210}Pb dating as well as benthic diatoms for cross-validation of chronological features within cored sediments of Lake Macquarie has not yet been reported for the lake.

5.2 Methods

A previous core collected for Wyee Bay provided assemblages (>1963) responding to plume temperatures of <3 °C above ambient. Analyses for heavy metals were not conducted for sediments of the core. While the core (1910-2003) adequately covered the period of power station operation (>1963), it did not contain “pre-industrial” sediments prior to the key date of 1897.

Benthic diatom assessments presented so far (chapters 2 and 3) have not provided evidence for a delineation of metal contamination-driven and thermal plume-driven assemblages. Although assemblage patterns associated with the plume were established, these were not isolated from other environmental variables, including Se. Modern assemblages were distinct for all three bays suggesting underlying environmental pressures contributing to inter-bay diatom variability. Also, an unexplained shift in assemblages was observed for the WB1C core within the period pre-dating Vales Point power station. Thus, additional cores from Wyee Bay, as well as the “control” bay, Crangan Bay, covering both post, pre-power station and pre-industrial periods of deposition at both sites were obtained.

A series of test cores collected from a shallow water (<2 m) area within 500 m of the Vales Point Power Station heated water discharge point (water temperatures >5 °C above ambient -

Chapter 2 – Ingleton and McMinn, 2012) in June 2009 indicated that a sediment depth of >35 cm could be achieved. For a sedimentation rate of 2.5 mm $year^{-1}$ (WBC1 at 21 cm Chapter 3), it was estimated that coring at this shallower site would yield sediments to an age of ~1870. In January 2010 the area was revisited and a sediment core of 54 cm was obtained (WBA) at 33' 09.2 °S 151' 31.9 °E. A core from a similar water depth at the southern end of Crangan Bay was also obtained (CBA) at 33' 9.6 °S 151' 35.8 °E to a sediment depth of 42 cm (Figure 5.1).

Sediments were collected using a modified passive gravity corer and removable 500 mm lengths of 74 mm diameter clear poly vinyl chloride (PVC) tubing. The top 10 cm of the core was extruded on site by subsampling at 0.5 cm intervals and transferring 5-10 g wet weight sediment from each subsection to individual sterile 50 mL high-density polyethylene (HDPE) centrifuge tubes. The remainder of the core was capped and transported back to the laboratory and later sub-sectioned at 1cm intervals (WBA 10-54 cm: CBA 10-42 cm). All sediment samples were stored in the dark at 2-4 ºC prior to analysis for ^{210}Pb, ^{7}Be and later diatom analyses. A 1 cm^3 subsample was retained and frozen at -18 ºC for heavy metal and organic matter (OM) analyses.

5.3.2 Sediment sample processing and analyses

5.3.2.1 Particle size and dry bulk density

Particle-size, bulk density and organic matter analyses were also conducted to normalise ^{210}Pb and heavy metal data and account for downcore sediment textural variability (Loring and Rantala, 1992). Analysis of sediment particle size was conducted for 20 subsamples from the WBA and CBA cores (Australian Nuclear Science and Technology Organisation - ANSTO method VI-3188). An aliquot of 0.5-1 cm^3 of sample was combined with 10 mL of water in a 20 mL glass vial and mixed by shaking and/or ultrasonicating. Organic matter (OM) was then removed by the addition of 1 mL of 10% H_2O_2 and heating the sample at ~ 60 °C until the reaction slowed. An additional 1 mL of 10% or 30% H_2O_2 was introduced to the sample (depending on vigour of the initial reaction) and the sample returned to the heat to remove any remaining OM. The sample was then allowed to cool before the addition of 1 mL 0.5 M Sodium Hexametaphosphate $(NaPO_3)_6$ and ultrasonicated for 15 minutes to disaggregate clay sized particles.

Particle size determination was conducted using a Malvern Mastersizer 2000 (Malvern Instruments Ltd., U.K.). A small amount of the pre-treated sample was added to 700 mL of reverse osmosis (RO) water in a 1 L beaker and ultra-sonicated before commencing sample measurement. This solution was introduced to the analyser and additional sample or RO water added to the beaker to until an obscuration value of between 10-20% was achieved. When median grain size d(0.5) readings fluctuated significantly the analysis was repeated by varying samples size, pump speed and/or level of ultra-sonification until a consistent value was achieved.

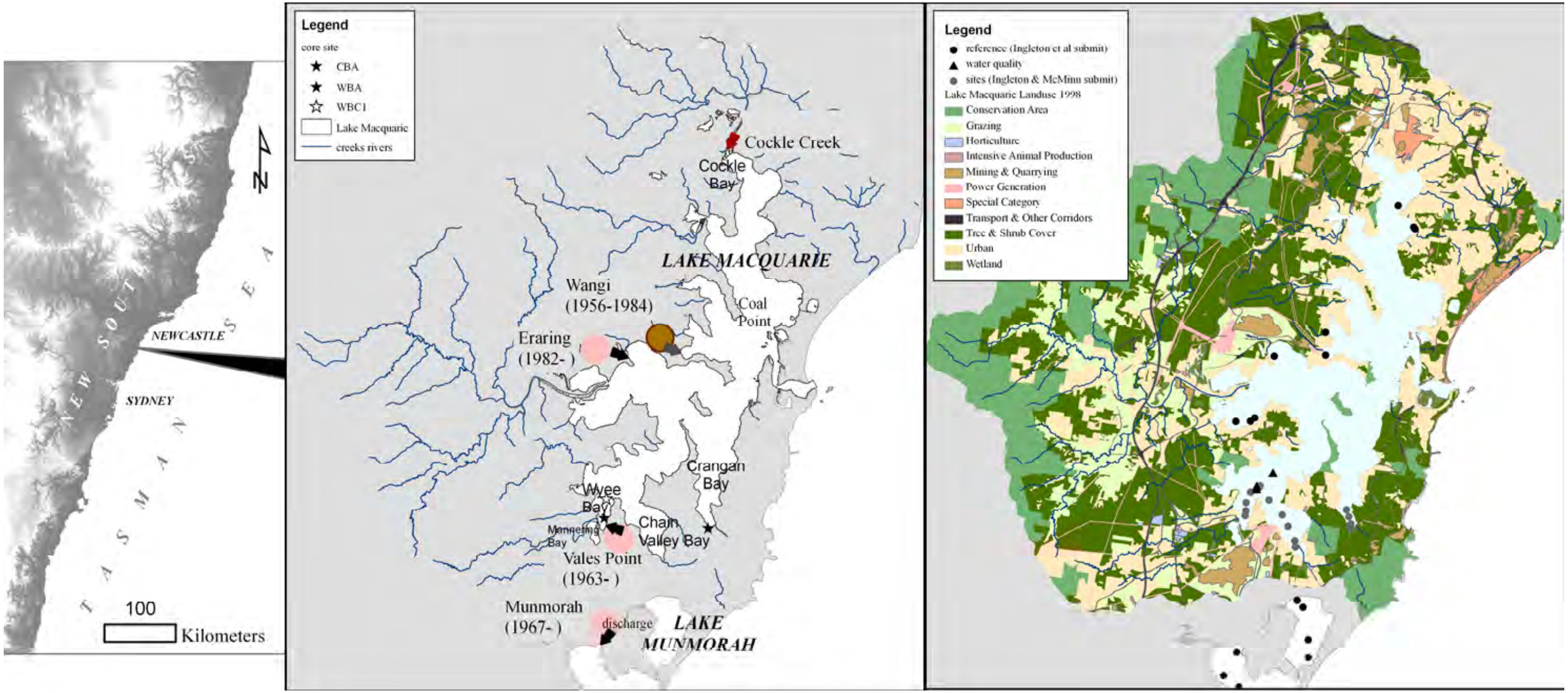
5.3.2.2 Organic matter

Percent organic matter (OM) for samples was determined by a Loss on Ignition technique. This involved the heated destruction of all OM and gravimetric determination of the relative sample weight loss (Schumacher, 2002). Between 4-10 g of wet sediment (equivalent to those depths for other analyses) was treated with 10% hydrochloric acid (HCl) to remove inorganic carbonates (~ 4 hrs), then dried at 107 °C. Samples were weighed and then fired overnight in a furnace at 550 °C. Once cooled, samples were transferred to desiccators and then re-weighed to determine relative weight loss.

Values were corrected for moisture content/inorganic carbon and OM values are presented as a percentage relative to initial sediment weight. Replicate samples indicated precision to be within ± 1% dry weight. The relative percentage of organic C in OM for Lake Macquarie sediments was not determined here and values are reported as % OM only. Total organic carbon (TOC) has been determined previously to be between 40-60% of OM within soils and sediments (Schumacher, 2002).

5.3.2.3 Heavy Metals

A total of 26 core sediment slices taken at regular intervals in both cores, CBA and WBA, were selected for aluminium (Al), Cd, chromium (Cr), cobalt (Co) Cu, iron (Fe), nickel (Ni), Pb, Se, vanadium (Vn) and Zn analyses. Between 0.5-2.5 g of wet sediment were weighed into 22 mL Teflon (Savillex) vials and dried at 107 °C for 2 hours. Dried samples were weighed, crushed to



i) ii) iii)

Figure 5.1 Location of i) Lake Macquarie; ii) Wyee Bay, Crangan Bay, core locations, power stations, smelter and Cockle Creek on the New South Wales Central Coast and; iii) spatial extent of broad land use categories for the lake's catchment in OEH (2008).

break up aggregated sediment particles and then reweighed prior to an addition of 10-15 mL aqua regia (75% nitric acid (HNO_3): 25% HCl). A total of 4 method blanks and 3 vials of 0.5-1 g of Standard Reference Material (SRM 2704 - Buffalo River marine sediments, National Institute of Standards and Technology, MD) were also prepared and aqua regia added. All vials were then heated on a heating block at 120-150 °C for a minimum of 4 hours.

Samples were allowed to settle and the supernatant diluted to a known volume before analysis using Inductively Coupled Plasma Mass Spectrometry (ICPMS). Three instrumental resolution settings low (LR), medium (MR) and high (HR) were employed during the analysis to overcome known interferences for some analyte metal spectra. Signal intensity decreases when moving from LR to MR to HR and for some elements, i.e. selenium, measurements in HR suffer from lower accuracy and precision. Indium (In) was used at a concentration of 100 ppb as an internal standard to monitor instrument performance during the sample sequence analysis and was typically between 98-109 ppb. For the SRM a recovery of 77 % to 102 % was achieved except for Al (23%), Cr (64%) and Vn (25%). The recovery values for these other metals, however, were consistent (±2 %) across all SRM replicates. The coefficient of variation for laboratory and blind replicates was less than 8% for all metals except Pb at 12%. Analytical detection limits were determined to be Al 10.0 µg g^{-1}, Cd 0.2 µg g^{-1}, Co 0.5 µg g^{-1}, and 1.0 µg g^{-1} for all other metals examined.

5.3.2.4 ^{210}Pb analysis

Bulk sediment samples were analysed for ^{210}Pb activity at the ANSTO Institute for Environmental Research using alpha spectrometry as per the ANSTO methods ENV-I-044-031/006/023 and 027 and described in McMinn et al. (1997) and Harrison et al. (2003). Samples were dried at 105 °C before being ground and passed through a 150 µm sieve. Approximately 5 g of dried sediment was weighed into a beaker and Pollodium-209 (^{209}Po) and Barium-133 (^{133}Ba) tracers and 25 mL of concentrated HNO_3 were added. The solution was then evaporated until dry. For the removal of OM, 25 mL H_2O_2 was added and allowed to effervesce in a water bath until the reaction ceased. Concentrated HCl (25 mL) was then added and the mixture refluxed in the water bath for a further

4-6 hours. The mixture was cooled and the sample centrifuged so the residue could be removed. Diethyl ether was then introduced to remove excess Fe and the sample evaporated until dry. The residue was then dissolved in 50 mL of 0.1 M HCl and ^{210}Po (+^{209}Po) autodeposited onto a silver disk by the addition of 1 g of the reducing agent (hydroxylammoniumchloride) and 100 mL citric acid to complex the metals Fe and Cr. Radium was co-precipitated with barium sulphate ($BaSO_4$) on a membrane filter source.

Activity of the sample on the silver disk ($^{210}Po/^{209}Po$ source) and membrane filter (Radium-226 (^{226}Ra) /^{133}Ba source) were counted by alpha spectrometry. The activity of the membrane filter was also counted using gamma-spectrometry to measure ^{133}Ba tracer activity. Chemical yield recoveries of ^{210}Po and ^{226}Ra were calculated using the recoveries of ^{209}Po and ^{133}Ba tracers. Resulting unsupported ^{210}Pb activities were modelled using both the Constant Initial Concentration (CIC) (Robbins, 1978) and the Constant Rate of supply (CRS) (Appleby and Oldfield, 1978) models and r-squared values calculated for each core profile.

5.3.2.5 ^{7}Be dating

^{7}Be dating (half-life of 53 days) of surface layers was employed to determine the dating inversion point to provide an indication of the extent of bioturbation/reworking or active mixing depth of the surface sediments. Samples for ^{7}Be analysis were dried, ground and sealed into petri dishes before counting by gamma-spectrometry. The analysis was performed only to determine the presence (or absence) of ^{7}Be peak at 477.6 keV in the gamma spectrometry spectrum for each sample. Samples were counted for between 1-5 days. No significant peak above background, however, was detected for any of the samples analysed.

5.3.2.6 Diatoms

A subset of core slice samples representing pre-metal contamination times in Crangan Bay were selected from the CBA core based on metal profiles. For fossil diatom analysis, approximately 1-2 g of wet sample was weighed into 50 mL HDPE plastic vials and treated with a cold digestion of 20-25 mL of 10% hydrogen peroxide (H_2O_2) for 48-72 hours to remove organic matter. The overlying supernatant was then siphoned off settled samples before the addition of 20-25 ml high purity water (0.2 µm filter), a broken coverslip and 5-10 drops of 5% glacial acetic acid to each vial. The contents of each vial were gently mixed before pipetting between 1–3 mL of suspended sediment onto cleaned 40 x 22 mm coverslips and left to dry in a dust free environment. Coverslips were then permanently mounted on pre-labelled glass slides using Norland Optical Adhesive 61 (Norland Products Inc., USA) and cured with ambient ultra-violet light (2-4 days).

Samples were examined under oil immersion at 1000 x magnification using a Leica DM2500 compound microscope with differential interference contrast (lens 100/1.25 oil) illumination. The microscope was equipped with a tri-focal head and a 10 megapixel Leica DFC480 digital camera controlled by Leica IM Version 4.0 digital imaging software (Leica Microsystems, Germany). A total of 400 or more individual diatom frustules on each slide were identified, where possible, to species level following recent scientific taxonomic literature (John, 1983; Saunders et al, 2010, Witkowski et al, 2007), and unpublished datasets (Taffs, 2005; Saunders, 2009). Only valves where greater than half the individual specimen was intact were counted in order to avoid counting the same specimen twice. Operator count error was determined by repeat counts on 6 slides producing a median error in relative abundance (RA) of ±0.63 % (n=178 species count comparisons). Slide preparation/sample heterogeneity estimated by counts on duplicate slides for four samples indicating a median RA error of ±1.36 % (n=91 species count comparisons) for species counts of >4 % RA.

5.4 Results

5.4.1 Dating Models

^{7}Be dating to determine the depth of the active sediment layer was unsuccessful here. The volume of material available was insufficient and subsequent layers were combined. Aspects of ^{7}Be analyses are not discussed further here other than that several cores or larger diameter cores would need to be acquired in the future to obtain adequate sample volume for the total suite of analyses.

Unsupported ^{210}Pb activities of sub-samples from the WBA core produced a mixed sediment profile, indicating that the sediment chronology was not well preserved and that the core was inadequate for dating and palaeoecological analysis (Figure 5.2a). The relatively noisy metal profile obtained for the WBA core was further evidence supporting the mixed nature of the sediments at that site. In comparison, ^{210}Pb activity within the CBA core had a trend of decreasing activity with depth and indicated it was suitable for dating. For CBA, unsupported ^{210}Pb ranged from 35.1 ± 1.9 Becquerel units (Bq) kg^{-1} at a depth of 0-0.5 cm to 4.5 ± 0.6 Bq kg^{-1} at a depth of 19-20 cm.

^{210}Pb activities equated to a CIC model (<63 µm fraction normalised data) age of 1926 and CRS (unaltered ^{210}Pb data) age of 1940 at 17-18 cm (Figure 5.2b). Mass accumulation rates were bimodal (0.14 g cm^{-2} y^{-1} 0-12 cm; 0.40 cm year^{-1} 12-20 cm) using the CIC model compared to the relatively consistent rates (0.19 to 0.27 g cm^{-2} y^{-1}) for the CRS model. Sedimentation rates were calculated as 2.09 mm y^{-1} for CIC and 2.51 mm y^{-1} for CRS. This equated to an 11-20 year difference between models at 19-20 cm and a 29-55 year difference at the bottom of the core. Particle size corrected unsupported ^{210}Pb activities exhibited some variability around a linear decay profile (r^2 = 0.85) indicating that sediment accumulation rates were not constant over time. The CIC and CRS models also differed somewhat with depth with CIC model uncertainties generally greater than those for the CRS model, except at the very surface. General agreement between CIC and CRS models would indicate constant mass accumulation rate over the period of core deposition and indicate that ^{210}Pb mostly entered the system from the atmosphere (A. Zawadski, pers. comm.). This was not the case in the CBA core. As CRS accounts for possible compaction within a core and changing sedimentation rates, it was selected as the preferred dating model.

5.4.2 Particle size, dry bulk density and organic matter

Particle size analyses indicated that mud (<63 µm fraction – defined as fine sand in IHO 14688-1) comprised >86 % for samples in the top 5 cm of the CBA core, of which 18-25% were clay sized (<2 µm) particles (Figure 5.3). At a depth of 11-12 cm the mud fraction declined to <50% and sand dominated cored sediments to a depth of at least 20 cm. While the dry bulk density in the hydrous surface layer (0-0.5 cm) was 0.3 g cm^{-3} the values for the remainder of the core described two distinct depth ranges. Generally, bulk density varied with textural properties and mud dominated sediments (0.73 -0.85 g cm^{-3}) lower than sand dominated sediments (1.02 - 1.19 g cm^{-3}). Following radio-isotope, metal and particle size analyses, an insufficient sediment volume remained for OM (LOI) analyses in the top 10 cm. A profile of OM concentrations (3.3 – 4.7 %) for 10-42 cm in the CBA core is presented in Figure 5.3.

5.4.3 Heavy Metals

Roach (2005) found Al adequate as a grain size normaliser in providing a significant regression model for assessment of the enrichment for Cu, Pb and Zn at Lake Macquarie sites. For Cd a raw background concentration of 0.2 was sufficient while for Se, both TOC and Al were required to obtain a significant regression model. Additional grain size normalisers (i.e. <63um fraction) was not required. For the CBA core, examined here, only the metals Cd, Cu and Zn concentration profiles showed a general trend of higher surface concentrations decreasing to relatively lower and more stable concentrations (background) at depth. For these metals, the trend was consistent for raw values as well as those normalised against the <63 µm fraction, OM and/or Al concentrations (Figure 5.4). Despite a mean recovery of 23%, consistency of the analyses across replicates indicated Al was adequate normaliser and was applied here. Concentrations of Cd, Cu and Zn reached maxima of 2.2 µg g^{-1}, 42 µg g^{-1} and 165 µg g^{-1}, respectively, in surface layers whereas background levels were 0.4 µg g^{-1}, 7 µg g^{-1} and 45 µg g^{-1}.

For Pb, Al-normalised concentrations were elevated toward the surface. Conversely, Pb was elevated at depth when normalised with the <63 µm fraction or OM. Selenium concentrations were variable (<1.1 µg g^{-1}). Se and all other metals analysed, however, were generally at or below background concentrations determined in previous studies.

A summary of Al-normalised metal concentrations in the CBA core and key dates for the introduction of historical metal sources to Lake Macquarie are presented in Figure 5.5. Generally,

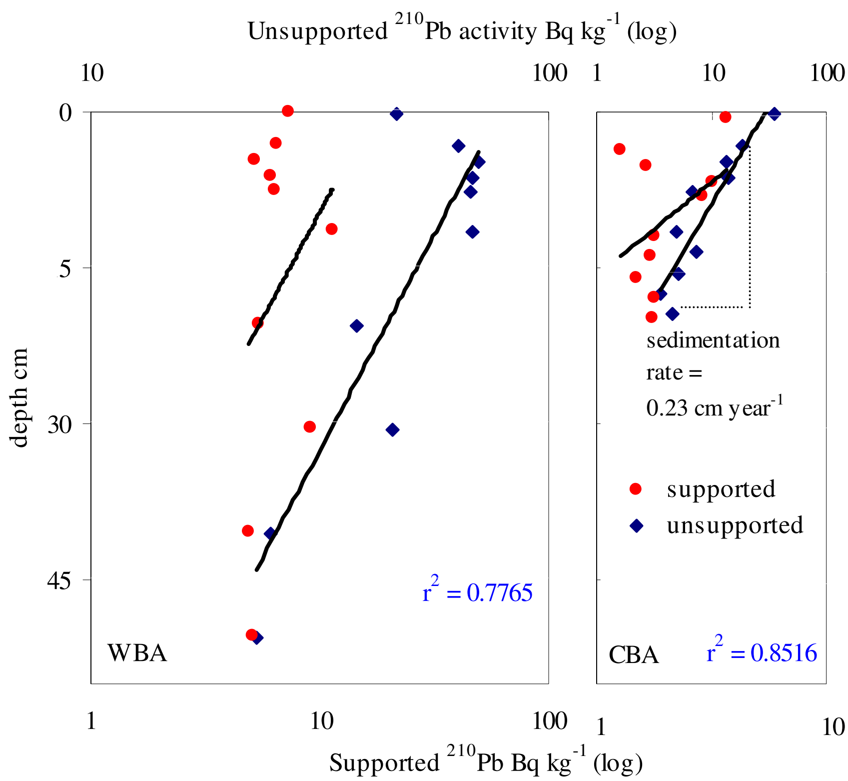


Figure 5.2a Particle size corrected, unsupported ^{210}Pb activity for cores sub-samples and linear fit r^2 values for cores WBA and CBA.

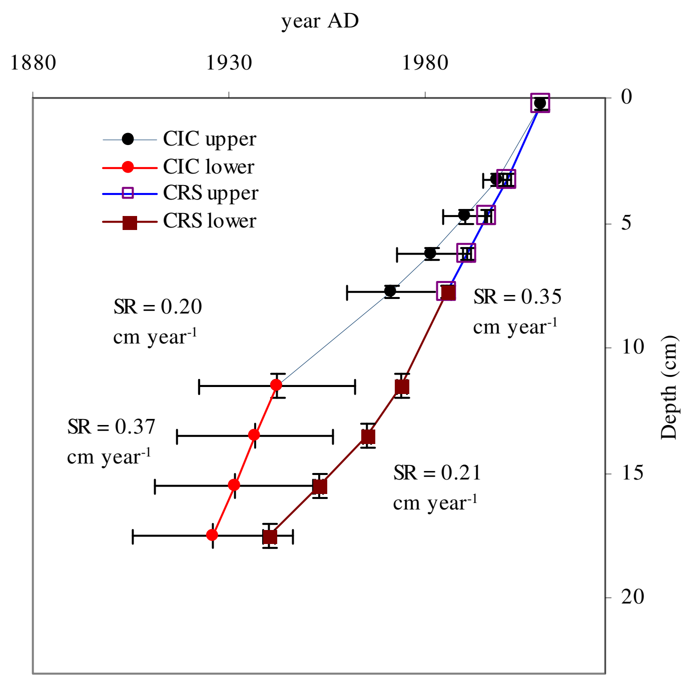


Figure 5.2b CRS and CIC models and sedimentation rates (SR) for core CBA.

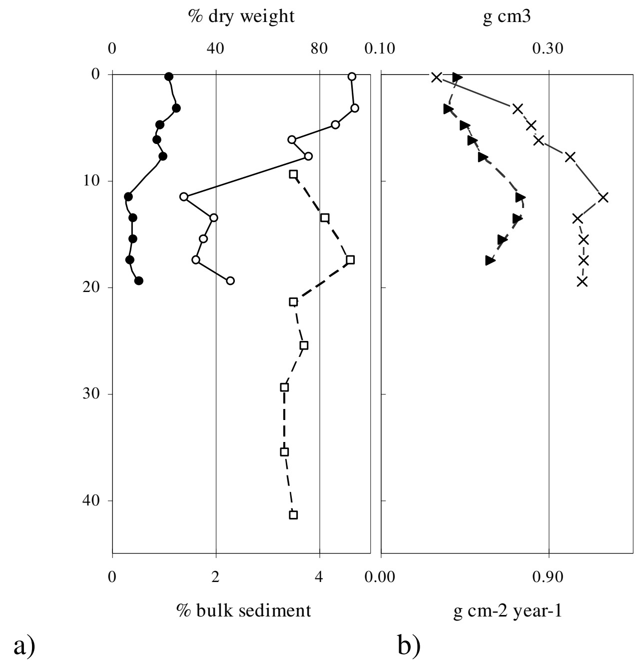


Figure 5.3 CBA core profiles of sediment textural properties for a) % organic matter (--□--), <63 µm fraction (-○-) and relative <2 um fraction (-●-); b) dry bulk density (-▶-) and CRS mass accumulation rate (-x-).

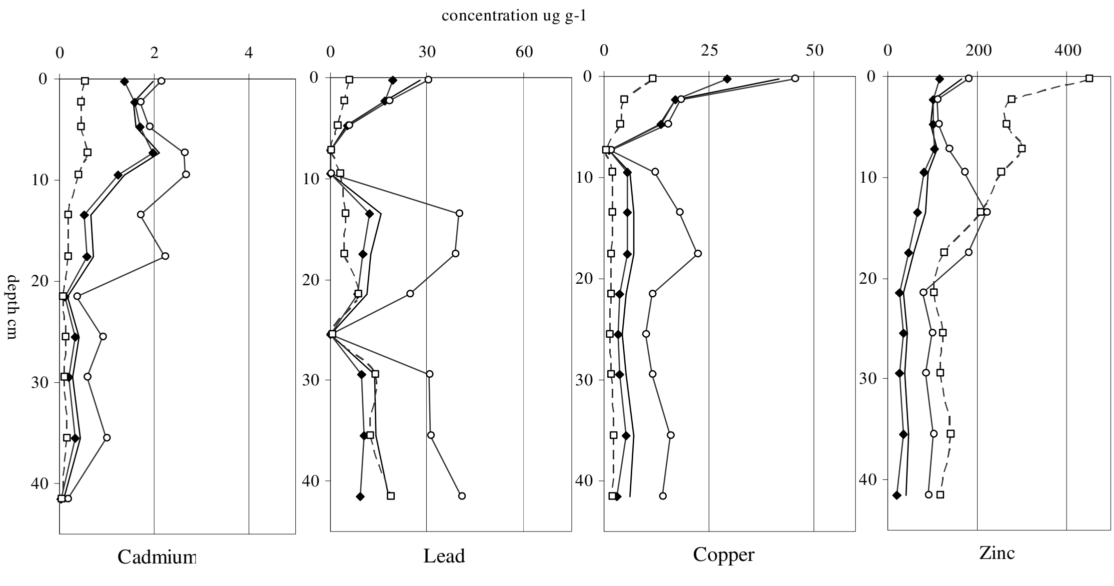


Figure 5.4 Concentration of metals with depth in core CBA as raw values (—) and normalised against Aluminium [/10000] (-◆-), <63 µm fraction [/100] (-○-) and % organic matter (--□--).

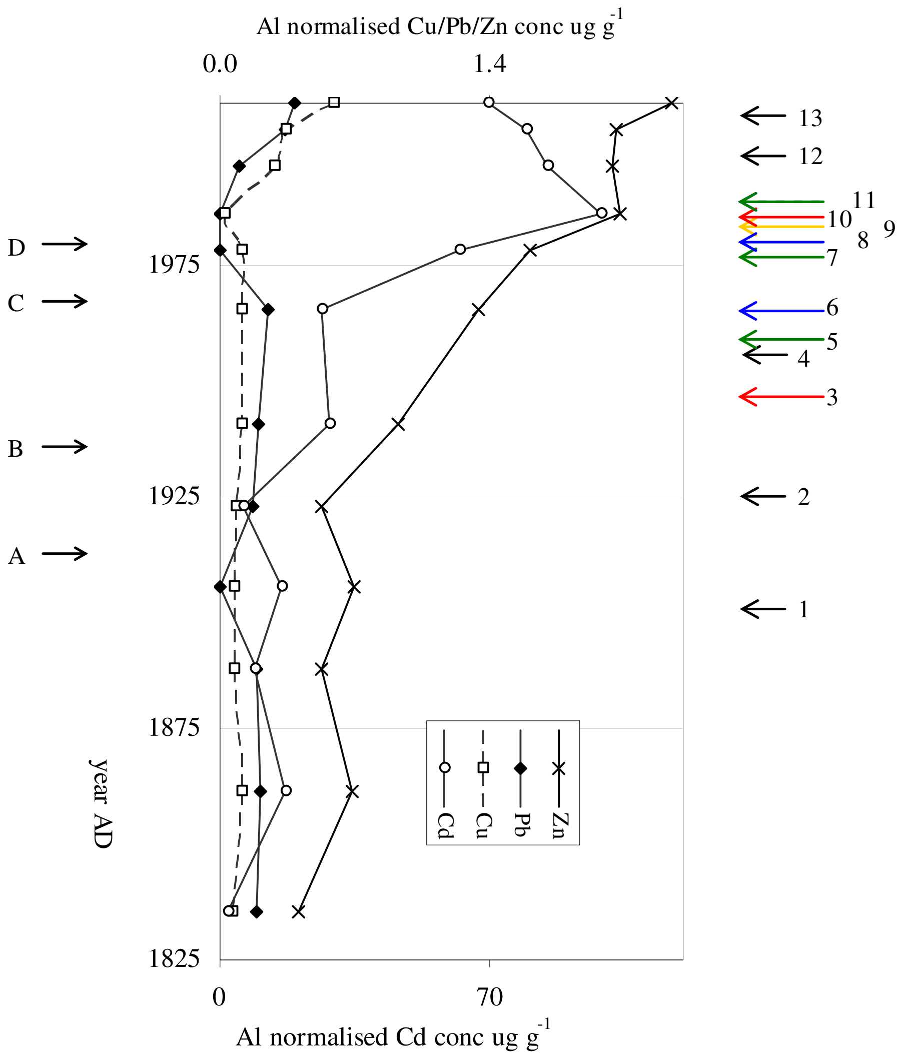


Figure 5.5 Al-normalised profiles for Cd, Cu, Pb and Zn, relative to CRS modelled dates for core CBA. Arrows indicate 1) smelter commissioning (1897), 2) smelter converted to chemical manufacture (1922), 3) commissioning of Wangi Power Station (1956), 4) revert to Pb-Zn smelting (1962), 5) comm. Vales Point Power Station (1963); 6) comm. Munmorah Power Station (1967); 7) upgrade Vales Point (1978); 8) downgrade Munmorah (1980); 9) comm. Eraring Power Station (1989); 10) close Wangi (1986) and 11) downgrade Vales Point (1989) and Munmorah (1990). Heavy metal horizons from Olmos and Birch (2010) are indicated as A) commencement of Pb-Zn enrichment core 3 (~1910); B) commencement of enrichment core 1 (~1940); C) Pb peak concentration core 3 (~1980), and D) Zn peak concentration core 3 (1990).

the metal profile for the CBA core showed distinct similarities to cores from other studies (Roy and Crawford 1984, Peters et al., 1999). This suggested that downcore variability in metal concentrations are reflective of source changes and not an artefact of site specific sediment chemistry or sediment metal mobility post burial (Olmos and Birch 2010).

5.4.4 Fossil diatoms

A total of six samples were selected from 20-42 cm sediment depth in the CBA core corresponding to samples selected for metal analyses and analysed for fossil diatoms. CBA species data was combined with data for the core WBC1 (Chapter 3) and then rarer species present at relative abundances (RA) <2% per sample or <5% across all samples were removed from the analysis. A total of 38 species retained and imported to CANOCO for analysis. Pie charts of RAs for 16 most common species for core CBA, WBC1 (Chapter 3) and select sites in surficial sediments of southern lake embayments (Chapter 2 – Ingleton and McMinn, 2012) are presented in Figure 5.6.

A Detrended Correspondence Analysis (DCA) on untransformed species data indicated that the gradient within the dataset was ~2.6 and, as a result, further exploration of the data utilised both linear and unimodal methods. A linear Principal Component Analysis (PCA) on log transformed and centred species data indicated that 75% of the variation within the dataset was explained for the first two principal axes compared to that using a unimodal Canonical Correspondence Analysis (CCA) with 66%. In both PCA and CCA samples basically fell into three broad groupings (Figure 5.5); 1) WBC1 (0.5-4.5 cm), 2) WBC1 (6-14 cm) and 3) WBC1 (17-21 cm) with CBA (20-42 cm) (Figure 5.7). Group 1 were characterised by species including *Paralia* sp., *Tryblionella lanceola*, *Navicula rhaphoneis* and *Cyclotella chocwhatcheeana*, Group 2 by variants of the species *Melosira sulcata*, *Trachyneis aspera* and *Gyrosigma* sp.6 and Group 3 by *Navicula robertsiana* and *Grammatophora* spp.

The removal of sample depths <12 cm (post-power station) for WBC1 from the analysis reduced the gradient of the dataset to <2. A PCA of the reduced dataset (n=16) indicated that 60%

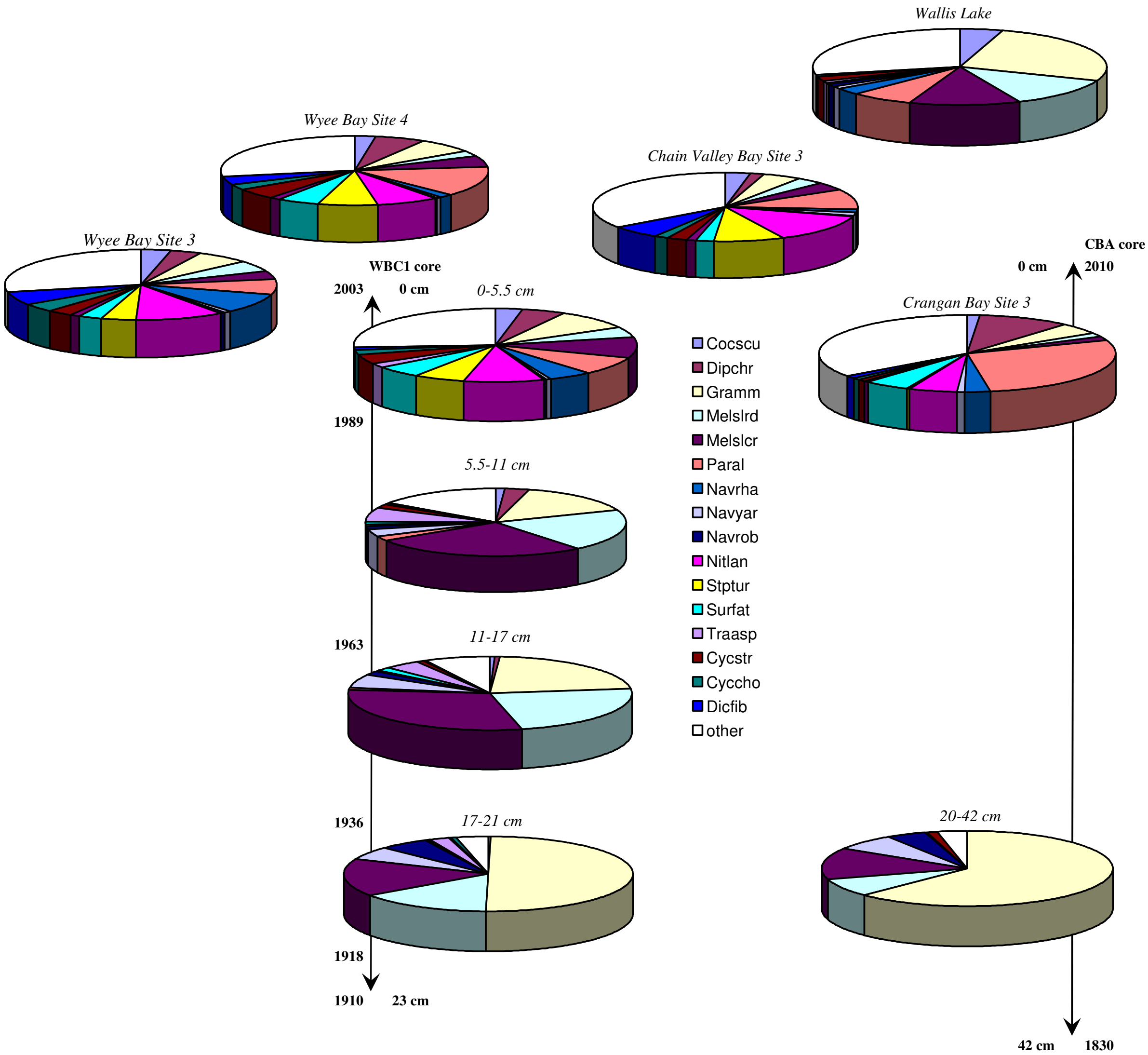


Figure 5.6 Pie charts of the 16 most common species for core CBA, WBC1 and select surficial sediment sampling sites in Wyee Bay, Chain Valley Bay and Crangan Bay.

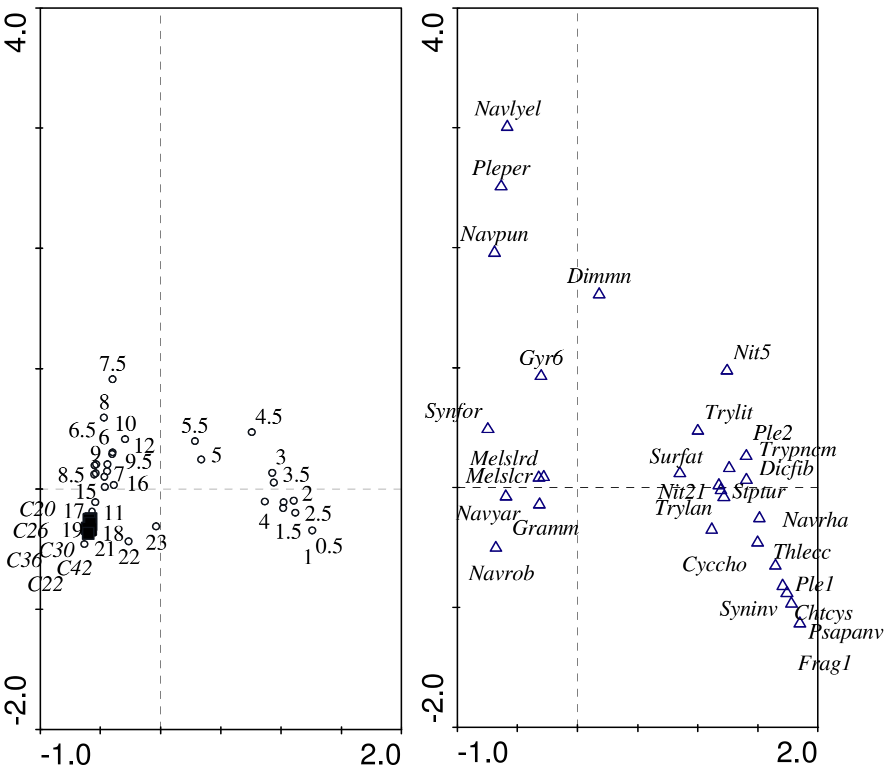


Figure 5.7 Samples and species plots of principal components for first and second axes from a CCA for all WBC1 core samples (circles) and slices for CBA core 20-42 cm (squares).

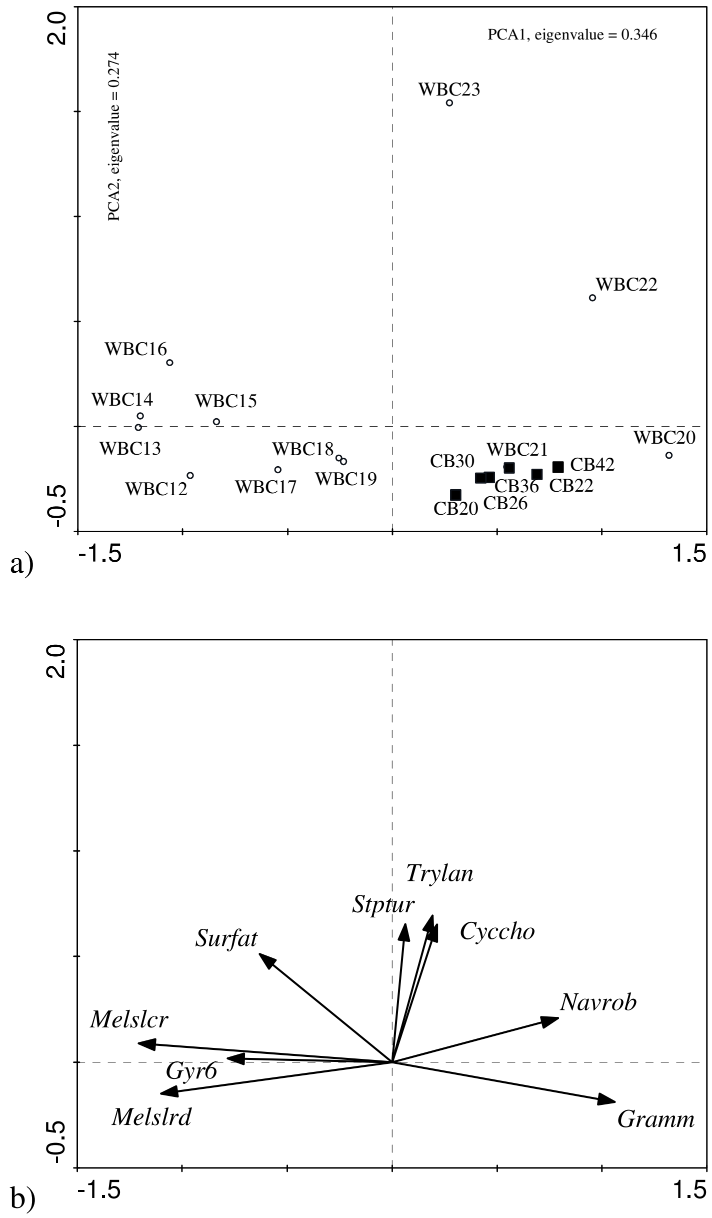


Figure 5.8 Plots of principal components for first and second axes from PCA for a) samples and b) species for core slices WBC1 12-23 cm (circles) and CBA 20-42 cm (squares).

of the variability between samples was explained by the first two principal components which increased to 80% with further reduction of the dataset to 29 species. For this scenario samples for WBC1 18-20 cm were most similar to CBA samples (Figure 5.8). Species characterising and driving the separation of these samples from other sites were the RA of *Navicula robertsiana* and *Grammatophora* spp.

5.5 Discussion

5.5.1 Event horizons and sediment chronologies

The data from the Crangan Bay core (CBA) was valuable in that it provided a "before-power station" assemblage at a control location that could be used for validating assemblage changes in the receiving bay core WBC1. Also, metal profiles obtained by previous studies in southern parts of Crangan Bay did not utilise ^{210}Pb dating techniques (core from Peters et al, 1999b was several km to the north off Nords Wharf) and focused validation efforts at sites in relatively more contaminated areas (Olmos and Birch, 2010). The work conducted here is the first time heavy metal, ^{210}Pb and fossil diatom data have been combined to cross-validate core chronology for the lake and provides new information on the history and potential mechanisms of metal enrichment at sites distant from major metal sources.

5.5.1.1 Sedimentation rates and the lake environment

The earliest sedimentation rates reported for Lake Macquarie sediments of 0.15-0.5 mm year^{-1} were based on radiocarbon dates (Roy and Crawford 1984) but were an order of magnitude smaller than more recent studies. Several studies examining sedimentation rates established rates of 6.2-8.3 mm year^{-1} based on fly ash (Chenhall et al, 1993 in AWACS, 1995), 1.5-5.0 mm year^{-1} based on metals (Batley, 1987), or 2.0-7.0 mm year^{-1} using multiple chemical markers (metal enrichment, tributyltin and organosilicons) (Kilby and Batley, 1993). These rates are more akin to recent work using ^{210}Pb dating and metal profiles with 4-14 mm year^{-1} at Cockle Bay (Olmos and Birch 2010) and 1.5-5.7

mm year at Nords Wharf (Peters et al, 1999b). For the cores obtained here, sedimentation rates were comparable reaching 1.8-4.2 mm year^{-1} in Wyee Bay (Chapter 2 – Ingleton and McMinn, 2012) and 1.6-4.7 mm year^{-1} at the southern end of Crangan Bay.

Apart from the use of the sedimentation rates for refining sediment chronologies, changes in rates of deposition may be indicative of changes in catchment processes. Increased sedimentation rates from lower to upper sections of cores have been reported for Cockle Bay, Wyee Bay and Nords Wharf are likely to reflect increased sediment loads to the lake as a result of land clearing and development of the lake's catchments (AWACS, 1995). In the north sedimentation rates increased in the 1950s (Olmos and Birch, 2010), however, for southern Crangan Bay sedimentation rates increased in-line with other southern lake core sites (Wyee Bay, Nords Wharf) around the 1980s. Sedimentation rates at the southern end of Crangan Bay increased despite the vegetated and relatively unmodified nature of the bay's immediate catchment. This is likely to indicate that sediment is likely to have been delivered to this site from across a broader lake area rather than from the sub-catchment and nearby creek.

5.5.1.2 Metal event horizons and smelter operations

Previous lake-wide studies of metals in surficial sediments identified Cockle Creek as the dominant point source of metal contamination to the lake (Roy and Crawford, 1984; Olmos and Birch, 2010) commencing with the commissioning of the Cockle Creek smelter in 1897. In 1922 the smelter plant changed its operational focus for a period to the manufacture of chemicals including super phosphate, fertilisers and sulphuric acid before reverting to smelting in 1962. Onsite treatment of sludge waste from the smelter initiated in the 1970's, was unsuccessful in preventing metals from continuing to enter northern lake sediments (Wilmore et al., 2006). The smelter ceased operation in 2003.

Elevated levels of heavy metals were first observed in northern lake sediments at Cockle Bay around 1910-1930 (Olmos and Birch, 2010). This was followed by increasing concentrations for Cd, Cu, Pb and Zn and then sustained high level (~ >5 x background) enrichment for >40 years.

During ~1940-1995 the metal profile was permeated by single or multiple peaks of Cd, Cu, Pb and Zn reaching >100x background for some metals (Olmos and Birch, 2010). In Crangan Bay to the south, enrichment of Cd and Zn in sediments (CBA core site) was first evident sometime after 1920-25 (21-22 cm) and before 1937-43 (17-18 cm) (Figure 5.5).

While peaks in both Cd and Zn were observed at both locations 1985-1995, concentrations of these metals with Crangan Bay sediments was <3% of that determined for Cockle Bay. Cd concentrations increased most significantly in Cockle Bay sediments from the 1970s when operations had reverted to smelting and reached ~140 $\mu g\ g^{-1}$ (~ 350 x background) around 1994 (Olmos and Birch, 2010). Concentrations of Cd at both locations have generally been in decline. Zn in Crangan Bay stabilised 1995-2003 at 85-95 $\mu g\ g^{-1}$ but has been followed by a more recent increase for 2003 to 2010 (Figure 5.5).

For Cu, concentrations increased significantly during 1922-1962 in Cockle Bay with a peak of >650 $\mu g\ g^{-1}$ around 1940 and a secondary peak of ~160 $\mu g\ g^{-1}$ ~1980 after smelting resumed (Olmos and Birch, 2010). This secondary peak in Cu coincided with peak Zn (>3500 $\mu g\ L^{-1}$), while peak Pb (>5000 $\mu g\ L^{-1}$) occurred earlier around 1968. For southern Crangan Bay, Cu enrichment within sediments did not become apparent until recently ~1990. Pb enrichment was not evident in surface sediments in 2010.

From the core chronology for Cockle Creek developed by Olmos and Birch (2010) the earliest smelting processes did not appear to deliver much in the way of immediate metal loads to sediments except, possibly Cu. It was during the period of chemical and fertiliser manufacture that significant loads of metals were first delivered to Cockle Bay sediments. While enrichment of Cockle Bay sediments at this time may have been the direct result of the discharge of wastes, alternatively, it may also have been the result of a redistribution of previously contaminated sediments from Cockle Creek to Cockle Bay (Olmos and Birch, 2010) or other additional localised sources.

Constituents of the wastes produced as a result of chemical manufacture at Cockle Creek are not known and monitoring of waters for metals did not commence until 1973 (SPCC, 1983).

Both Cd and Pb have been identified as constituents of mineral and organic based fertilisers (Mortvedt, 1996) and contamination of sediments with Cd, Cu, As and Zn attributed to sulphuric acid and chemicals manufacture has been identified elsewhere (Spliethoff and Hemond, 1996). Regardless, from the chronologies described here and in relation to previous work, for Crangan Bay sediments both Cd and Zn appear to have been sourced from contamination within the northern lake.

5.5.1.3 Alternative metal sources

Significant alternative potential sources of metals to the lake did not appear until commissioning of coal-fired power stations at Wangi in (1956-1986), Vales Point in (1963-), Munmorah (1967-) and Eraring (1982-) (Figure 5.1). Previous studies had identified power stations as relatively localised sources of a range of metals of which Se associated with fly ash has been studied most thoroughly (Peters et al, 1999a; Peters et al, 1999b). Metal enrichment of Zn and Cu in cored sediments has been linked with fly ash deposition at nearby Lake Munmorah (Batley et al., 1990), Zn and Pb have been associated with operations at Eraring (Chenhall et al, 1993), Pb with power station cooling water discharges and Cu/Cd with fly ash from Wangi (Roy and Crawford, 1984).

For southern Crangan Bay, enrichment of Cd and Zn in sediments was already evident by the time the first station on the shores of the lake was commissioned. Background concentrations of Se and Pb indicate that this southern extent of the bay lies distant from sources such as power station cooling water discharges and ash dam runoff (water-borne fly ash). CBA sediments did not appear to be suffering from delayed secondary redistribution of these metals through lake circulation processes.

The delivery of metals associated with airborne fly ash to Crangan Bay, however, would be relatively immediate delivered directly via atmospheric fallout. Zn, Cd and Cu enrichment at the Crangan Bay core site commenced 20-30 years prior to the commissioning of the two nearest power stations of Vales Point (5 km west) and Munmorah (8.5 km south-west). By the time Cu reached levels greater than background (1990s) in the CBA core, Eraring (10 km north-west) was online but operation at Wangi (12 km north-northwest) had ceased and capacity at Vales and Munmorah had been downgraded. Batley (1987) identified fly ash as a source of metals to lake sediments but dismissed the contribution as relatively minor. Although there was an increase in the concentrations for Zn and Cd following commissioning of these power stations, a signal associated with a contribution of these metals from fly ash can not truly be delineated from metal contributions from other metal sources.

Municipal sewage discharged to the lake increased significantly in volume from the 1950-60s until effluent was diverted to ocean outfalls in 1994 (AWACS, 1995). For sewage Zn is the metal of greatest interest (Batley, 1987). In Lake Macquarie discharges were concentrated in the northern sections of the lake and although they may have acted as a source, their contribution to lake wide distribution of Zn is unknown. Localised sources of metals to Crangan Bay are limited as the immediate catchment is predominantly vegetated, that apart from some roads and a small quarry, is dominated by vegetated landscape and a conservation area (Figure 5.1). Some urban development lies to the north (1.5-2 km) along the eastern and western shores of the bay and may be contributing as a more recent metal source.

Historically urban development has generally been concentrated across catchments of the northern lake and the suburbs of Newcastle. More recent development in the south and west, including the shores of Crangan Bay, since the 1980s, is likely to be contributor of metals to the lake (Delacruz, pers. comm.). Despite this, Cd, Pb and Zn still described strong north to south decreasing trends in 2003. Cu enrichment was generally relatively more widespread than the other metals and likely the result of urban sources (Roy and Crawford, 1984; Olmos and Birch, 2010).

5.5.4 Metals and secondary redistribution

Metal contamination appears to be a continuing legacy for the sediments and ecology of Lake Macquarie. In 2010 at Crangan Bay, sediments were enriched by ~2.5x, 3-4x and 4-5x that of background concentrations for Cd, Cu and Zn, respectively. This equated to increases of 62 % for Cu and 14 % Zn since 2003 at the site.

Event horizons identified in the CBA core were aligned or slightly offset when compared to horizons for the same metals in cores from Cockle Bay. With strong north-south gradient for Cd, Pb and Zn (Olmos and Birch, 2010) this indicates that metals in sediments of the northern lake are the most likely source for metal enrichment in southern Crangan Bay. For Cd and Zn initial enrichment and peaks in concentrations occurred in Crangan Bay within 5-10 years of that observed for Cockle Bay. Zn is considered the most mobile metal when compared to other major metals (Cd, Cu, Pb, Se) in Lake Macquarie (Roy and Crawford 1984).

Previous studies have suggested that Cd is a relatively immobile metal, readily sedimented and likely derived from localised sources (Roy and Crawford, 1984). Low level enrichment (<2 $\mu g\ g^{-1}$) in sediments of the CBA during 1920-30s indicate otherwise. The bay is relatively non-urban and localised source of Cd are unlikely. Studies of metal mobilisation with changes in pH and redox in contaminated sediments indicate that sulphide bound Zn and Cd to be more easily mobilised than Pb and Cu (Calmano et al, 1993). For estuarine sediments, however, metal mobilisation is complex and not yet fully resolved (Simpson et al, 1998). With concentrations in Cockle Bay 25x and 75x that of Crangan Bay sediments, Cd may well have been redistributed from the northern to southern lake on similar time frame and mechanism to that for Zn.

By comparison, both Cu and Pb in CBA sediments did not conform, with or without a time offset, to the profile pattern from the northern lake core 3 (Olmos and Birch, 2010) suggesting the smelter was not a direct source for these metals across this distance. Although the north-south gradient in Pb concentrations was evident in 1975 and 2003, redistribution processes do not appear to have taken the metal as far as the southern end of Crangan Bay (2010). Roy and Crawford (1984) indicated that Cu and Pb were generally less transportable compared to Zn for Lake Macquarie. Although concentrations in sediments of Cockle Creek and Cockle Bay were extreme (Roy and Crawford, 1984; Olmos and Birch, 2010) particularly for Pb (>3000 µg g-1), both Cu and Pb do not appear to have responded in the same way as Zn and Cd in their re-distribution. Distribution is likely to have been controlled by factors including initial concentrations decreasing as a function of distance, hydrological constraints on lake circulation (Roy and Crawford 1984), differing behaviours in metal species, smelter operational regimes, production volumes and waste metal loads.

5.5.3 Earlier low level enrichment or metal remobilisation?

Generally, enriched metal species, concentrations and down core profiles are similar in sediments of the CBA core to other southern lake cores analysed by Olmos and Birch (2010) in 2003 (Core 1 – Crangan Bay) and by Roy and Crawford (1984) near Summerland Point (Core 25). Most notably for the 2003 core, the break point (point of greatest change in concentration) for Cd, Cu, Pb and Zn occurred at a comparable depth (~2.5-3 cm sedimentation 2003 to 2010 - @ 0.63 cm $year^{-1}$) to that in CBA when compared at the same depth resolution (i.e. a greater depth resolution was achieved for the CBA core). While ^{210}Pb dating was conducted on the CBA core but not Core 1, the more recent core was limited to 42 cm and a maximum age of ~1835 compared to a Core 1 depth of 107-108 cm. For this earlier and longer core a smaller but notable trend of increasing concentrations can be observed for a greater background period (Olmos and Birch, 2010). Both Pb and Zn appear to increase from a point at a depth of ~42 cm (2010 equivalent of ~43-44 cm with 7 years sedimentation @ 0.23 cm $year^{-1}$) for Core 1 that in the CBA core indicates low level enrichment to a date of at least ~1830. Cores from northern and southern lake sites in other studies (Cores 10 & 25 in Roy and Crawford 1984) show similar low level enrichment trends suggesting that diffuse metal contamination may have been an issue prior to commissioning of the smelter.

Sources to the lake pre-smelter are not discussed widely in the literature. The presence of black coal and its significance to the Hunter area, however, is well known. Coal is NSW's greatest export at a value of $11.2 billion dollars 2009-10 (NSW Department of Trade and Investment, 2011). 89% (NSW Minerals Council, 2011) of primary energy production for the state is derived from coal compared to 54% for the country (ABS, 2008). Coal mining operations commenced on the western shores of Lake Macquarie around 1841 at the Ebenezer coal works at Coal Point (National Library of Australia: www.trove.nla.gov.au) and at least 6 separate collieries had operated within the lake's catchment to 1960 (S. Walpole, pers. comm.). Coal mining and operations such as coal washing, loading and transportation may well have contributed metals to the lake in earlier times.

This period of lower level enrichment has generally not been discussed in detail within the literature as levels are in the range of 1-2x background and considered to be non-significant or within the realm of analytical sensitivity. The feature, however, is consistent across sites and studies and does not appear to be attributable to a change in sediment textural or geochemical attributes that would otherwise be more site specific. Peters (1999b) attributed low level enrichment at depth to a "bleeding" of metal concentrations from adjacent overlying layers with relatively higher concentrations through a process of metal remobilisation. Such a mechanism would be, however, limited to the depth of the oxic layer at any point in time as anoxic conditions make metals relatively immobile (Calmano et al., 1993). In the case of Se, metal ions bind with sulphide and forms compounds such as selenite and selenate (Peters et al., 1999b). Remobilisation requires changes to the sediment redox potential usually as a result of bioturbation and/or sediment resuspension that result in a disrupted sediment chronology.

For the CBA core in this study, the ^{210}Pb profile remained intact and if remobilisation was a factor then it would have been limited to a vertical distance less than that between two adjacent dated depth slices. A ^{210}Pb profile analysis interval of 1.5-3.5 cm for the core translated to a maximum dating error of ~16.5 years (3.5 cm at 0.21 cm year^{-1}). Variability in the core dating models based on unsupported ^{210}Pb and sediment textural errors, however, limited dating errors to < ±1.5 years (over depths of 3-20 cm) or equivalent to ~6 mm (core average) according to the CRS model.

Bioturbation can exceed depths 10-20 cm in the muddy sediments of these estuarine systems. In its absence, however, the oxic layer is usually limited to 2-5 mm (Simpson et al, 1998). The limited volume of sediment in subsamples for ^{7}Be analysis meant that determination of surface layer mixing was unsuccessful and ^{210}Pb sub-sampling resolution meant that the dating inversion point could not be determined adequately. If confidence in the CRS ^{210}Pb dates is valid and remobilisation is considered not an issue then the lower level enrichment (<1-2 x background) at depth (~40-65 cm Core 1 Olmos and Birch, 2010) for 60 or more years prior to smelter operation, may be considered a realistic feature of the sediment profile. With respect to fossil diatoms, remobilisation of metals is likely restricted to a scale of surface reworking and in-situ post-burial geochemical changes are unlikely to alter buried assemblages.

5.5.5 Selenium, other metals and benthic lake ecology

Several studies of metals in Lake Macquarie have focused on Se as an indicator of metal contamination from power stations arising from fly ash entering the environment and becoming incorporated into lake sediments (Peters et al., 1999a; Jasonsmith et al., 2008). Water samples collected from Mannering Lake ash dam ~1987 found Se concentrations similar to that for unpolluted waters and suggesting that ash dam water was not a source of Se (Batley, 1987). Se, however, was more broadly elevated in sediments of Mannering Bay, Wyee Bay and Chain Valley Bay (Peters et al, 1999a). A peak in Se concentrations around late 1980s-early 1990s and subsequent decline may be reflective of changes to management of ash dam runoff. Since 1996 ash dam water is recycled and likely to have reduced the contribution of this as a metal source to Mannering Bay sediments (Peters et al, 1999b).

Controls on air borne particulates in stack emissions have only recently been employed with the installation of filters in 2006 (Scrivener, pers. comm.). Peters et al. (1999a) indicated Se to be elevated in surface sediments of Crangan Bay at Nords Wharf at a peak of ~1.5 µg g-1 at 20 cm (detection limit of 0.2 $\mu g\ g^{-1}$). In this study, the lower sensitivity of the HR setting for Se detection using ICPMS, variability in SRM recoveries and poorer analytical detection limit for Se (~ ±0.5 $\mu g\ g^{-1}$) resulted in a noisy Se profile indistinguishable from background.

Benthic diatom community composition has been used as an indicator of anthropogenic metal contamination in coastal sediments in Antarctica (Cunningham et al, 2005) and freshwater streams in the USA (Crossey and LaPoint, 1988; Ivorra et al., 1999). Previous multi-taxa studies for Lake Macquarie indicated that Cd then Pb and Zn were significant variables governing the assemblages of benthic macrofauna within the lake (Simpson et al., 2005). For the benthic diatom work conducted here, metals are enriched sediments of both the control and receiving water bay (Roach, 2005) and are likely a contributing factor for benthic diatom distribution of the southern lake. While studies have reported Cu, Ag and Se to be the main metals of concern for sediments in Wyee Bay (Peters et al., 1999a; Roach, 2005), Cu, Zn and Cd appear to be the metals of concern for southern sections of Crangan Bay. Attributing modern or fossil diatom assemblages to concentrations and/or combinations of metals in sediments for the lake was not achieved here.

5.5.6 Fossil diatoms and pre-industrial water quality of Lake Macquarie

A reconstruction of the environmental variables using diatom-inferred models applied to the diatom data (Chapters 3 and 4) for the CBA core was not conducted here. Pre-metal contamination diatom assemblages in Crangan Bay, however, were most similar to those assemblages dated pre-1935 followed by pre-power station assemblages (1935-1963) in the Wyee Bay (WBC1) core (Chapter 2 – Ingleton and McMinn, 2012). This indicated that a common benthic diatom flora occupied these embayments prior to ~1935 (17 cm) in Wyee Bay (Chapter 2 – Ingleton and McMinn, 2012) and at least as late as ~1925 (20cm) in Crangan Bay (this study). Thus, sediments at depth in the CBA core and possibly the WB1C core appear to represent periods prior to 1930s metal enrichment (>2-3x background) for the southern lake. An intact chronology, metal and diatom analyses of a core from Wyee Bay would have provided an opportunity to validate this.

According to the diatom analysis, floral diversity during ~1800-1935 was greater and consisted of predominantly larger (>40-50 μm) species compared to relatively smaller and diverse range of species in modern assemblages for both bays (Chapter 3). The change in size range, however, does not appear to be associated with depth as a function of sediment texture, burial/compaction or frustule dissolution that may be considered a factor for small or less robust planktonic species. Relatively smaller and/or less robust species including *Cyclotella striata*, *Cocconeis scutellum* and *Cocconeis pseudomarginata* were present at depth to maximum RAs of 6%. Similarly, while some large species were present throughout the core (*Grammatophora* spp.

Melosira sulcata and *Navicula yarrensis*), changes in large species with depth were also apparent with *Gyrosigma* sp.1 and *Trachyneis aspera* present in surface layers but absent at depth.

In relation to the status of past water quality the addition of CBA core diatom data does not provide new information. It provides, however, an indication that the past environment of Wyee Bay, with lower salinities and water temperatures but equivalent orthophosphate concentrations relative to 2003, is also likely to also have been characteristic of Crangan Bay. Thus, pre-industrial lake conditions in Wyee Bay may have covered a greater area and been consistent across the lakes southern embayments (including Chain Valley Bay). Conditions appear to have been consistent for Crangan Bay to at least 1790-1835 (projected date for CBA 42 cm based on sedimentation rate at 20 cm).

Unfortunately, the shell layer at 21-23 cm in core WBC1 and disrupted chronology for core WBA and prevented the analysis of deeper sediments in Wyee Bay. Modern day assemblages in Crangan Bay may be indicative of surficial metal contamination with Cd, Cu and Zn. They differed from modern day Wyee Bay assemblages (Chapter 2 – Ingleton and McMinn, 2012) from sediments enrichment with Cu, Ag and Se (Roach, 2005). If metals delivered to sediments of Crangan Bay from the northern lake were also delivered to Wyee Bay at around the same time, pre-1935 assemblages in WBC1 would be indicative of conditions of pre-metal contamination and prior to power station commissioning. It is predicted that metal profiles of a core collected from Wyee Bay and with an adequately preserved chronology would see down core Se concentrations approach background concentrations around 1963 while Zn (and other metals) would approach background some 20-40 years earlier around 1935.

5.5.7 Further work

A complete analysis of diatoms preserved within samples of the CBA core is required to fully explore the relationship between assemblages and metal concentrations over time for Crangan Bay. A change in metal concentrations ~1985 highlights an event horizon of potential significance for the Crangan Bay environment.

In Wyee Bay, the period leading up to 1963 and commissioning of the Vales Point power station was relatively stable (1920-40). The shift in assemblages was most likely attributable to the presence of the thermal plume (Chapter 3); however, it was likely to have occurred against an underlying relatively low level metal enrichment arising from the northern lake. Once commissioned, a slightly different suite of metals associated with fly ash and/or ash dam runoff is then also likely to have become a factor. Only with the analysis of cores from other non-impacted coastal systems could the temporal changes in assemblages across this time span be validated.

5.6 Conclusions

^{210}Pb dating combined with heavy metal profiles within sediments of Crangan Bay analysed here provided evidence for the onset of anthropogenic contamination to this section of the lake to between 1920-1943 with Cd and Zn. Although Cu contamination is relatively more recent Cu (since 1980), metal enrichment is potentially a factor contributing to the distribution of benthic diatoms in Crangan Bay.

Determination of a metal profile and cross-validation with ^{210}Pb dating for the control bay provided a greater understanding of the mechanisms of contaminant dispersal throughout the lake over time. Zn and possibly Cd contamination from the northern lake appears to have been redistributed to the far southern section of the lake over timescales of 5-10+ years. For Cu, redistribution has either occurred over a longer time frame (20-40 years) or is the result of more relatively modern sources. Although concentrations of metals are in general decline, historic metal contamination in sediments of the northern lake is a continued legacy for the system and its ecology.

Combined with the diatom assemblage data, dating and heavy metal information for the CBA core provided a means to pinpoint and cross-validate the pre-industrial period for Crangan Bay. If this contaminant horizon can be inferred for other southern sections of the lake then the data might assist in delineating pre-power station and pre-industrial assemblages within core WBC1 in Wyee Bay. Together the assemblage data from both cores indicated that pre-industrial lake conditions were similar for both bays. During pre-industrial times the environments within these embayments experienced lower median salinities and water temperatures but similar orthophosphate concentrations compared to that of the modern lake.

6. Thesis Conclusions

The work contained within this thesis presents a novel approach for the determination of spatial and temporal change in an estuarine lake embayment affected by a thermal discharge from a power station. It was determined that not only were diatoms responding to the thermal plume in the modern day environment but they also shifted in association with changes to the temperature regime within the receiving embayment and in line with different phases of power station operation. While initial temperature-inference models were limited to delineating long-term trends, they indicated that the temperature regime was cooler prior to power station commissioning. The change was not discernable, however, from regional climatic changes that had also taken place across the same time frame.

Further development of reference datasets involved sampling across a temperature gradient over a larger geographical area and resulted in improvements to temperature reconstructions. A nested and evenly sampled dataset provided the best predicted temperature history relative to long-term monitoring and temperature proxy data. This established that the diatom-inferred temperature history was a reflection of changes to the bay's temperature regime and associated with the power station discharge as opposed to that of regional scale changes in temperature. Average water temperatures in Wyee Bay were ~21.5 °C prior to the power station discharge.

Chronologies determined for the most recent core obtained within the control embayment, Crangan Bay, indicated heavy metal contamination was pervasive and distributed lake-wide by ~1925. Thus, metal contamination may have been a factor that contributed to a shift in the ecology of Wyee Bay at a similar time. This could not be validated by an additional Wyee Bay core obtained during the final field campaign. A comparison of diatom assemblages between bays indicated that Wyee Bay and Crangan Bay experienced similar conditions prior to sediment metal enrichment to at least ~1790.

The work presented here demonstrates the applicability of the palaeoecological and multi-taxa assessment techniques for assessing the effects of point source thermal discharges to NSW estuaries. The approach can be used to establish baseline conditions where pre-industrial information on system health is lacking. The methods enable environmental managers to determine the scale and direction of change within coastal systems exposed to a complex suite of natural and anthropogenic based pressures. These tools will prove to be of increased value for improved understanding and management of estuaries with additional pressures associated with an altering climate.

7. References

Agbeti, M.D., 1991. Relationship between diatom assemblages and trophic variables: A comparison of old and new approaches. Canadian Journal of Fisheries and Aquatic Sciences 49, 1171-1175.

American Public Health Association, 1998. Standard methods for the analysis of water and wastewater, 20th edition. American Public Health Association, Water Environment Federation, American Water Works Association, Washington, U.S.A. ISBN 0-87553-235-7: 1,220 pp.

Anderson, N.J., 1993. Natural versus anthropogenic change in lakes: the role of the sediment record. Trends Ecol. Evol. 8, 356-361.

Anderson, N.J., 2000. Diatoms, temperature and climate change. European Journal of Phycology 35, 307-314.

Andren, E., 1999. Changes in the composition of the diatom flora during the last century indicate increased eutrophication of the Oder Estuary, south-western Baltic Sea. Estuarine, Coastal and Shelf Science, 48:665-676.

Anraku, M., 1974. Review – warm water effluents and plankton. Bulletin Plankton Society Japan 21: 1-31.

Appleby PG, Oldfield, F, 1978. The calculation of ^{210}Pb dates assuming a constant rate of supply of unsupported ^{210}Pb to the sediment. Catena 5, 1–8.

Australia and New Zealand Environment and Conservation Council (ANZECC)/Agriculture and Resource Management Council of Australia and New Zealand (ARMCANZ), 2000. Paper 4: Water Quality Benchmarks: Australian water quality guidelines for fresh and marine waters. Commonwealth Department of Sustainability, Environment, Water, Population & Communities, http://www.environment.gov.au/.

Australian Water and Coastal Studies Pty. Ltd., 1995. Lake Macquarie estuary process study Volume 1 Report. Prepared for Lake Macquarie Council in conjunction with JH Laxton and ES Laxton Pty Ltd, AWACS report 94/25, Nov. 1995, 170pp.

Bamber, R., 1995. The influence of rising background temperature on the effects of marine thermal effluents. Journal of Thermal Biology 20, 105-110.

Bamber, R.N., Spencer, J.F. 1984. The benthos of a coastal power station thermal discharge canal. Journal Marine Biological Association of the United Kingdom 64, 603-623.

Banks, S.C., Ling, S.D., Johnson, C.R., Piggott, M.P., Williamson, J.E., Beheregaray, L.B., 2010. Genetic structure of a recent climate change-driven range extension. Molecular Ecology 19, 2011-2024.

Batley, G.E., 1987. Heavy metal speciation in waters, sediment and biota from Lake Macquarie, NSW. Aust. J. Freshwater Research 38, 591-606.

Batterbee, R.W., 1986. Diatom analysis. P. 527-570. In: B.E. Berglund (ed.), Handbook of Holocene Palaeoecology and Palaeohydrology. John Wiley and Sons Pty. Ltd., Chichester, United Kingdom.

Batterbee, R.W., Kneen, M.J., 1982. The use of electronically counted microspheres in absolute diatom analysis. Limnology and Oceanography, 27:184-188.

Batterbee, R.W., Jines, V.J., Flower, R.J., Cameron, N.G., Bennion, H., Carvalho, L., Juggins, S., 2001. Diatoms: In: Smol, J.P., Birks, H.J.B., Last, W.M., (eds), Tracking Environmental Change Using Lake Sediments. Volume 3: Terrestrial, algal, and siliceous indicators, Kluwer Academic Publishers, Dordrecht, The Netherlands, pp/ 155-202.

Bayliss, D., 1973. Marine fouling organisms in Lake Macquarie and the Tuggerah Lakes, NSW. MSc thesis University of New South Wales.

Beaugrand, G., 2004. The North Sea regime shift: evidence, causes, mechanisms and consequences. Progress in Oceanography 60, 245-262.

Bender, E.A., Case, T.G., and Gilpin, M.E., 1984. Perturbation experiments in community ecology: theory and practice. Ecology, 65: 1-13.

Barwick, M., Maher, W., 2003. Biotransference and biomagnification of selenium, copper, cadmium, zinc, arsenic and lead in a temperate seagrass ecosystem from Lake Macquarie Estuary, NSW, Australia. Marine Environmental Research 56, 471-502.

Bilger, C., Hall, R.I., 2003. Diatoms as quantitative indicators of July temperature: a validation attempt at century-scale with meteorological data from northern Sweden. Palaeogeography, Palaeoclimatology and Palaeoecology 189, 147-160.

Birch, G.F., 2000. Marine pollution within Australia, with special emphasis on central New South Wales estuaries and adjacent continental margin. International journal of environment and pollution 13, 573-607.

Birch, G.F., Ingleton, T.C., Taylor, 1997. Environmental implications of dredging in the world's second largest coal exporting harbour, Port Hunter, Australia. Journal of Marine Engineering 4, 135-145.

Birch, G.F., Taylor, S, 1999. Source of heavy metals in sediments of the Port Jackson estuary, Australia. Science of the Total Environment 227, 123-128.

Birks, H.J.B., 1998. Numerical tools in paleolimnology – progress, potentialities, and problems. J Paleolimnology 20, 307-322.

Boyd, R., Ruming, K., Goodwin, I., Sandström and Schröder-Adams, C., 2008. Highstand transport of coastal sand to the deep ocean: A case study from Fraser Island, southeast Australia. Geological Society of America 36, 15-18.

Boylen, C.W., Brock, T.D., 1973. Effects of thermal additions from the Yellowstone Geyser Basins on the benthic algae of the Firehole River. Ecology 54, 1282-1291.

Brando, V.E., Dekker, A.G., 2003. Satellite hyperspectral remote sensing for estimating estuarine and coastal water quality. IEEE Transactions on Geoscience and Remote Sensing 41, 1378-1387.

Brugam, R.B., 1978. Pollen Indicators of Land-Use Change in Southern Connecticut. Quaternary Research 9, 349-362.

Burt, A., Maher, W., Roach, A., Krikowa, F., Honkoop, P., Bayne, B., 2006. The accumulation of Zn, Se, Cd, and Pb and physiological condition of *Anadara trapezia* transplanted to a contamination gradient in Lake Macquarie, NSW, Australia. Marine Environmental Research 64, 54-78.

Cai, W., Shi, G., Cowan, T., Bi, D. and Ribbe, J. 2005. The response of the southern annular mode, the East Australian Current, and the southern mid-latitude ocean circulation to global warming. Geophysical Research Letters, 32(23), pp 1-4. ISSN 0094-8276

Calmano, W., Hong, J. and Förstner, U., 1993. Binding and mobilisation of heavy metals in contaminated sediments affected by pH and redox potential. Water Science and Technology, 28(8-9): 223-235.

Cameron, N.G., 1995. The representation of diatom communities by fossil assemblages in a small acid lake. Journal of Paleolimnology 14, 185-223.

Casal, G., Kutser, T., Dominguez-Gomez, J.A., Sanchez-Carnero, N., Freire, J., 2011. Mapping benthic macroalgal communities in the coastal zone using CHRIS-PROBA mode 2 images. Estuarine, Coastal Shelf Science 94, 281-290.

Chapman, M.G., Underwood, A.J., Skilleter, J.A., 1995. Variability at different spatial scales between a subtidal assemblage exposed to the discharge of sewage and 2 control assemblages. J. Exp. Mar. Biol. Ecol. 189, 103-122.

Chen, C., Shi, P., Mao, Q., 2003. Application of remote sensing techniques for monitoring the thermal pollution of cooling-water discharge from a nuclear power plant. Journal of Environmental Science and Health, Part A – Toxic/Hazardous Substances and Environmental Engineering A38, 1659-1668.

Chenall, B.E., Organ, M., Jones, B.E., 1993. Lake Macquarie Environmental Research Report. Geology Department, University of Wollongong.

Chessman, B., 1999. Rapid assessment of rivers using macroinvertebrates: A procedure based on habitat specific sampling, family level identification and a biotic index. Australian Journal of Ecology 20, 122-129.

Chessman, B., Growns, I., Currey, J., Plunkett-Cole, N., 1999. Predicting diatom communities at the genus level for the rapid biological assessment of rivers. Freshwater Biology 41, 317-331.

Chuang, Y., Yang, H., Lin, H., 2009. Effects of thermal discharge from a nuclear power plant on phytoplankton and periphyton in subtropical coastal waters. Journal of Sea Research 61, 197-205.

Cremer, H., Sangiorgi, F., Wagner-Cremer, F., McGee, V., Lotter, A.F., Visscher, H., 2007. Diatoms (Bacillariophyceae) and dinoflagellate cysts (Dinophyceae) from Rookery Bay, Florida, U.S.A. Caribbean Journal of Science 43, 23-58.

Cremer, H., Melles, M., and Wagner, B., 2001. Holocene climate changes reflected in a diatom succession from Basaltsø, East Greenland. Canadian Journal of Botany 79, 649-656.

Crosby, L.H., Wood, E.J.F., 1959. Studies on Australian and New Zealand diatoms, II – Normally epontic and benthic genera. Transactions of the Royal Society of New Zealand 86, 1-58.

Crossey, M.J., La Point, T.W., 1998. A comparison of periphyton community structure and functional responses to heavy metals. Hydrobiologia 162, 109-121.

Crosta, X., Romero, O., Armand, L., Pichon, J. 2005. The biogeography of major diatom taxa in Southern Ocean Sediments: 2. Open ocean related species. Palaeogeography, Palaeoclimatology and Palaeoecology 223, 66-92.

Cooper, S., Gaiser, E., Wachnicka, A., 2010. Estuarine paleoenvironmental reconstructions using diatoms. In: Smol, J.P., Stoermer, E.F., The Diatoms: Applications for the Environmental and Earth Sciences. Cambridge University Press, United Kingdom. pp.686.

Cummins, S., Roberts, D., Murray, S., 2009. Seagrass and macroalgal survey, summer 2009. Project Number ECOBSGAR – 407248. Bioanalysis Pty Ltd, Final Report Eraring Energy.

Davies, W.A., Linkson, P.B., 1991. Selenium discharge from power station ash dams: Eraring, Vales point. Quantity, speciation and strategies for control. Department of chemical Engineering, University of Sydney.

Dela-Cruz, J., Pritchard, T, Gordon, G., Ajani, P., 2006. The use of periphytic diatoms as a means of assessing impacts of point source inorganic nutrient pollution in south-eastern Australia. Freshwater Biology 51, 951-972.

Delft, 1970. Gold Coast Queensland Australia – Coastal erosion and related problems. Report 257, Delft Hydraulics Laboratory.

Department of Climate Change and Energy Efficiency, 2009. Climate change risks to Australia's coast: A first pass national assessment. Commonwealth of Australia, 2009 ISBN 978-921298-71-4

Dickman, M. and Glenright, T., 1997. A comparison of marine planktonic and sediment core diatoms in Hong Kong with emphasis on *Pseudo-nitzschia*. Hydrobiologia 352, 149-158.

Digby, M.J., Saenger, P., Whelan, M.B., McConchie, D., Eyre, B., Holmes, N., Bucher D., 1999. A physical classification of Australian estuaries. Report prepared for the urban water research association of Australia by the Centre for Coastal Management Southern Cross University 16/99, Lismore NSW.

Dixit, S.S., Smol, J.P., Kingston, J.C., Charles, D.F., 1992. Diatoms: powerful indicators of environmental change. Environmental Science and Technology, 26: 22-23.

Queensland Department of Environment and Natural Resources, 2010. Ecosystem Health Monitoring Program – South-east Queensland Health-e-waterways program, Network database, 2010.

Eisma, D., Berger, G.W., Wei-Yue, C., Jian, S., 1989. Pb-210 as a tracer for sediment transport and deposition in the Dutch-German Waddensea. In: Proceedings KNGMG Symposium, Coastal Lowlands. Geology and Geotechnology, 1987, pp. 237-253.

Electricity Commission of New South Wales, 1983. Report on the effects of heated water discharges from power stations on the environments of Lake Macquarie and Tuggerah Lakes, Power Development Division Report PD92, March 1983, 60pp.

Esper, O., Gersonde, R., Kadagies, N., 2010. Diatom distribution in southeastern pacific sediments and their relationship to modern environmental variables. Palaeogeography, Palaeoclimatology and Palaeoecology 287, 1-27.

Eyre, B., 2005. Lake Macquarie Water Quality Review 2001-2005. Report for the office of the Lake Macquarie Catchment Coordinator, Eraring Energy and Delta Electricity, Report Number CCB2005-04, Lake Macquarie Council, Australia.

Facca, C., Sfriso, A., 2007. Epipelic diatom spatial and temporal distribution and relationship with the main environmental variables in coastal waters. Estuarine, Coastal and Shelf Science 75, 35-49.

Finkel, Z.V., Beardall, J., Flynn, K.J., Quigg, A., Rees, T.A.V., Raven, J., 2010. Phytoplankton in a changing world: cell size and stoichiochemistry. Journal of Plankton Research 32, 119-137.

Fisher, R.A., A.S. Corbet, C.B. Williams, 1943. The relationship between the number of species and the number of individuals in a random sample of an animal population. Journal of Animal Ecology 12, 42-58.

Flannery, T. 1994. The Future Eaters: An ecological history of the Australasian lands and people, Reed Books, Melbourne, 303 pp.

Friedlander, J.C., 1980. A study of the fish community in the *Zostera capricorni* beds of Myuna Bay in Lake Macquarie, NSW. MSc thesis University of New South Wales.

Fritz, S.C., Juggins, S., Batterbee, R.W., Engstrom.,D.R., 1991. Reconstruction of past changes in salinity and climate using a diatom-based transfer function. Nature 352, 706-708.

Gale, E., Pattiaratchi, C., Ranasinghe, R., 2006. Vertical mixing processes in Intermittently Closed and Open Lakes and Lagoons, and the dissolved oxygen response. Estuarine, Coastal and Shelf Science 69, 205-216.

Gasse, F., and Tekaia, F., 1983. Transfer functions for estimating paleoecological conditions (pH) from East African diatoms. Hydrobiologia 103, 85-90.

Gasse, F., Juggins, S. and Ben Khaelifa, L., 1995. Diatom-based transfer functions for inferring past hydrochemical characteristics of African Lakes. Palaeogeography, Palaeoclimatology, Palaeoecology 117, 31-54.

Gaul, U., Geissler, U., Henderson, M., Mahoney, R., Reimer, C.W., 1993. Bibliography on the fine-structure of diatom frustules (Bacillariophyceae). Proceedings of The Academy of natural Sciences of Philadelphia 144, 69-238.

Gell, P.A., 1997. The development and application of a diatom calibration set for lake salinity, western Victoria, Australia. Quaternary Australasia, 15, 43-44.

Gibbons, D.E., Wukelic, G.E. Leighton, J.P. Doyle, M.J., 1989. Application of landsat thematic mapper data for coastal thermal plume analysis at Diablo Canyon. Photo-grammetric Engineering and Remote Sensing 55, 903-909.

Gillanders, B.M., Elsdon, T.S., Halliday, I.A., Jenkins, G.P., Robins, J.B. and Valesini, F.J., 2011. Potential effects of climate change on Australian estuaries and fish utilising estuaries: a review. Marine and Freshwater Research, 62, 1115-1131.

Growns, I.O., Growns, J.E., 2001. Ecological effects of flow regulation on macroinvertebrate and periphytic diatom assemblages in the Hawkesbury-Nepean River, Australia. Regulated Rivers: Research and Management 17, 275-293.

Gutteridge, Haskins and Davey 1992. The effects of power station cooling water discharge upon the benthos of Lake Macquarie. Part A: Biological report. Report prepared for Pacific Power.

Haese, R.R., Murray, E.J., Smith C.S., Smith, J., 2007. Diatoms control nutrient cycles in a temperate, wave-dominated estuary (southeast Australia). Limnology and Oceanography 52, 2686 -2700.

Hallegraeff, G., Hosja, W., Knuckey, R. and Wilkinson, C., 2008. Recent range expansion of the red-tide dinoflagellate *Noctiluca scintillans* in Australian coastal waters. IOC-UNESCO Harmful Algae Newsletter 38, 10-11.

Harris, G.P., 2001. Biogeochemistry of nitrogen and phosphorus in Australian catchments, rivers and estuaries: effects of land use and flow regulation and comparisons with global patterns. Marine and Freshwater Research 52, 139-149.

Harrison, J., Heijnis, H., and Capriella, G., 2003. Historical pollution variability from abandoned mine sites, Greater Blue Mountains World Heritage Area, NSW, Australia. Environmental Geology 43, 680-687.

Hayes, D.E. and Ringis, J. 1973. Seafloor spreading in the Tasman Sea. Nature 243, 454-458.

Heap, A., Bryce, S., Ryan, D., Radke, L., Smith, C., Smith, R., Harrie, P. & Heggie, D., 2001. Australian Estuaries and Coastal Waterways: A Geoscience Perspective for Improved and Integrated Resource Management, A report to the National Land & Water Resources Audit (NLWRA) Theme 7: Ecosystem Health. Geoscience Australia Record 2001/07, Geoscience Australia, Canberra.

Hedger, R.D., Malthus, T.J., Folkard, A.M., Atkinson, P.M., 2007. Spatial dynamics of estuarine water surface temperature from airborne remote sensing. Estuarine Coastal and Shelf Science 71, 608-615.

Hein, M.K., Koppen, J.D., 1979. Effects of thermally elevated discharges on the structure and composition of estuarine periphyton diatom assemblages. Estuarine and Coastal Marine Science 9, 385-401.

Hickman, M., 1974. Effects of the discharge of thermal effluent from a power station on Lake Wabamun, Alberta, Canada – The epipelic and episammic algal communities. Hydrobiologia 45, 199-215.

Hickman, M., 1982. The removal of a heated water discharge from a lake and the effect upon an epiphytic algal community. Hydrobiologia, 87: 21-32.

Hickman, M. and Clarer, D.M., 1975. The effect of the discharge of thermal effluent from a power station on the primary productivity of an epiphytic algal community. Br. Phycol. J. 10, 81-91.

Hodgson, D.A., Wright, S.W., Tyler, P.A., Davies, N., 1998. Analysis of fossil pigments from algae and bacteria in meromictic Lake Fidler, Tasmania, and its application to lake management. J. Paleolimnol. 19, 1-22.

Hobday, A.J., Okey, T.A., Poloczanska, E.S., Kunz, T.J. & Richardson, A.J. (eds) 2006, Impacts of Climate Change on Australian Marine Life: Part B Technical Report, report to the Australian Greenhouse Office, Canberra.

Holland, V.M., 1982. The effects of some environmental of the growth and viability of *Zostera capricorni* Asherson. MSc thesis, Univ. of New South Wales.

Hickman, M., 1974. Effects of the discharge of thermal effluent from a power station on Lake Wabamun, Alberta, Canada – The epipelic and episammic algal communities. Hydrobiologia 45, 199-215.

Ingleton, T.C., McMinn, A., 2012. Thermal Plume Effects: A multi-disciplinary approach fro assessing the effects of thermal pollution on estuaries using benthic diatoms and satellite imagery. Coastal, Estuarine and Shelf Science 99, 132-144.

Ivorra, N., Hettelaar, J., Tubbing, G.M.J., Kraak, M.H.S., Sabater, S., Admirall, A., 1999. Translocation of microbenthic algal communities used for in situ analysis of metal pollution in rivers. Arch. Environ. Contam. Toxic 37, 19-28.

Jasonsmith, J.F., Maher, W., Roach, A.C., Krikowa, F., 2008. Selenium bioaccumulation and biomagnification in Lake Wallace, New South Wales, Australia 59, 1048-1060.

John, J., 1983. The diatom flora of the Swan River Estuary Western Australia, Vol. 64, Bibliotheca Phycologia, Vaduz.

Johnston, E.L. (2011). Tolerance to contaminants: Evidence from chronically exposed populations of aquatic organisms. In: Tolerance to Environmental Contaminants ed. by C Amiard-Triquet, PS Rainbow and M Romeo. CRC Press.

Kelly, M.G., 1998. Use of assemblage-based metrics to monitor eutrophication in European rivers. Environmental Conservation 25, 22-29.

Keskitalo, J., 1987. Phytoplankton in the sea area off the Olkiluoto nuclear power station, west coast of Finland. Annals Botanici Fennici 24, 281-299.

Kilby, G.W., Batley, G.E., 1993. Chemical indicators of sediment chronology. Australian Journal of Marine and Freshwater Research 44, 635-647.

Kirby, J., Maher, W., Krikowa, F., 2001. Selenium, cadmium, copper and zinc concentrations in sediments and mullet (*Mugil ceaphalus*) from the southern basin of Lake Macquarie, NSW, Australia. Arch. Environ. Contam. Toxicol. 40, 246-256.

King, R.J., Hodgson, B.R., 1986. Aquatic angiosperms in coastal saline lagoons of New South Wales: IV. Long-term changes. Proceedings of the Linnean Society of NSW 109, 51-60.

Kingston, J.C., Birks, H.J.B., Uutala, A.J., Cumming, B.F., Smol, J.P., 1992. Assessing trends in fishery resources and lake water aluminium fro paleolimnological analyses of siliceous algae. Can. J. Fish. Aquat. Sci 49, 116-127.

Kocha, M.S. Schopmeyera, S.A., Nielsena, O.I., Kyhn-Hansena, C., Madden, C.J., 2007. Conceptual model of seagrass die-off in Florida Bay: Links to biogeochemical processes. J. Experimental Marine Biology and Ecology 350, 73-88.

Kott, P., 1955. The zooplankton of Lake Macquarie 1953-1954. Australian Journal of Marine and Freshwater Research 6, 429-442.

Kromkamp, J.C., de Brouwer, J.F.C., Blanchard, G.F., Forster, R.M., Creach, V., 2006. Functioning of microphytobenthos in estuaries. Royal Netherlands Academy of Arts and Sciences, Amsterdam, the Netherlands, pp. 262. ISBN 90-6984-453-2.

Lake Macquarie City Council, 1997. Lake Macquarie estuary management study: Volume 2 – Lake Management Issues. Prepared by WBM Oceanics Pty Ltd, Spring Hill, QLD. Rep. 00016787:9487.R5.4, pp. 193.

Langford, T.E.L., 2001. Thermal Discharges and Pollution. In: Thorpe, S.A., Turekian, K.K. (eds), Encyclopaedia of Ocean Sciences 6, Elsevier Science Ltd. 2001, pp. 2933-2940.

Lardici, C., Rossi, F., Maltagliati, F., 1999. Detection of Thermal Pollution: Variability of benthic communities at two different spatial scales in an area influenced by a coastal power station. Marine Pollution Bulletin 38, 296-303.

Leterme, S.C., Ellis, A.V., Mitchell, J.G., Buscot, M.J., Pollet, T., Schapira, M., Seuront, L., 2010. Morphological flexibility of *Cocconeis placentula* (Bacillariophyceae) nanostructure to changing salinity levels. J. Phcology 46, 715-719.

Logan, B., Taffs, K., 2011. The Burrum River estuary: Identifying reference sites for Australian sub-tropical estuarine systems using paleolimnological methods. Journal of Paleolimnology 46, 613-612.

Logan, B., Taffs, K.H., Eyre B.D., Zawadski, A., 2011. Assessing changes in nutrient status in the Richmond River estuary, Australia, using paleolimnological methods. Journal of Paleolimnology 46, 597-611.

Lough, JM, 2009. Temperature. In: A Marine Climate Change Impacts and Adaptation Report Card for Australia 2009 (Eds. E.S. Poloczanska, A.J. Hobday and A.J. Richardson), NCCARF Publication 05/09, ISBN 978-1-921609-03-9.

Lovett, G., Burns, D.A., Driscoll, C.T., Jenkins, J.C., Mitchell, M.J., Rustad, L., Shanley, J.B., Likens, G.E., Haeuber, R., 2007. Reviews: Who needs environmental monitoring. Frontiers in Ecology and the Environment 5, 253-260.

MacIntyre, R.J., 1959. Some aspects of the ecology of Lake Macquarie, NSW with regard to an alleged depletion of fish. VII: The benthic macrofauna. Australian Journal of Marine and Freshwater Research 10, 341-353.

MacIntyre, R.J., Holliday, R.J., 1993. Lake Macquarie zooplankton – Stage 2 (1975-1991). Report prepared for Pacific Power, Unisearch Limited.

Mahoney, R.K., Reimer, C.W., 1997. Updated status of the type collection (Bacillariophyceae) in the diatom herbarium, The Academy of Natural Sciences of Philadelphia. Proc. of the Nat. Acad. Sci. Phil. 147, 125-192.

Makridakis S, Wheelwright SC, Hyndman RJ (1998) Forecasting: Methods and applications, Third edition. John Wiley and Sons, N.Y.

Mallin, M.A., Stone, K.L., Pamperl, M.A., 1994. Phytoplankton community assessments of seven southeast U.S. cooling reservoirs. Water Research 28, 665-673.

Marmorino, G.O., Smith, G.B., 2008. Thermal remote sensing of estuarine spatial dynamics: Effects of bottom-generated vertical mixing. Estuarine, Coastal and Shelf Science 78, 587-591.

Masscheleyn, P.H., Delaune, R.D., Patrick, W.H., 1991. Arsenic and selenium chemistry as affected by sediment redox potential and pH. J. Environ. Qual. 20, 522-527.

McMinn, A., 1992. Quaternary coastal evolution and vegetation history of northern New South Wales, Australia, based on dinoflagellates and pollen. Quaternary Research, 38:347-358.

McMinn A, Hallegraeff GM, Thomson P, Jenkinson AV, Heijnis H, 1997. Cyst and radionucleotide evidence for the recent introduction of the toxic dinoflagellate *Gymnodinium catenatum* into Tasmanian waters. Mar. Ecol. Prog. Ser. 161, 165–172.

McMinn, A., Heijnis, H., Murray, A., Hallegraeff, G.M., 2003. Diatom and dinoflagellate assemblages of the Hawkesbury River, N.S.W., over the last two centuries: evidence for changes in hydrology, Alcheringa 28, 505-514. ISSN 0311-5518 (2004)

Mortvedt, J.J., 1996. Heavy metal contaminants in inorganic and organic fertilisers. Fertiliser Research 43, 55-61.

Moser, K.A., MacDonald, G.M., Smol, J.P., 1996. Applications of freshwater diatoms to geographical research. Progress in Physical Geography 20, 21-52.

Mustard, J.F., Carney, M.A., Sen, A., 1999. The use of satellite imagery to quantify thermal effluent impacts. Estuarine, Coastal and Shelf Science 49, 509-524.

New South Wales Office of Environment and Heritage (NSW OEH), 2009. Environment Protection Licence Number 761 for Delta Electricity, Vales Point Power Station and Coal Unloader, Mannering Park. 19 July 2009, pp. 29.

New South Wales State Fisheries, 1981. The impact of Munmorah power station on the recreational and commercial finfish fisheries of Tuggerah Lakes.

Nichol, S.L., 2001. Chapter 18 – Value of estuarine sediments for understanding natural environmental change in coastal regions. In: Eds. Gostin, V.A. - Gondwana to greenhouse: Australian Environmental Geoscience, Australian Geological Society of Australia Special Publication Sydney, Australia, no.21, pp 356. ISBN 1876125225.

Niemi, G., Wardrop, D., Brooks, R., Anderson, S., Brady, V., Paerl, H., Rakocinski, C., Brouwer, M., Levinson, B., McDonald, M., 2004. Rationale for a new generation of indicators for coastal waters. Environmental Health Perspectives 112, 979-986.

Olmos, M.A., Birch, G.F., 2010. A novel method using sedimentary tools and GIS for measuring anthropogenic change in coastal lake environments. Environmental Science Pollution Research 17, 278-287.

Parsons, M.L., Turner, R.E. and Rablais, N.N., 1999. Salinity histories of coastal marshes reconstructed from diatom remains. Estuaries 22, 1078-1089.

Peierls, B., Paerl, H.W., in press. Longitudinal and depth variation of bacterioplankton productivity and related factors in a temperate estuary. Estuarine, Coastal and Shelf Science pp.1-9.

Peters, G.M, Maher, W.A., Krikowa, F., Roach, A.C., Jeswani, H.K., Barford, J.P., Gomes, V.G., Reible, D.D., 1999a. Selenium in sediments, pore waters and benthic infauna of Lake Macquarie, NSW, Australia. Marine Environmental Research 47, 491-508.

Peters, G.M., Maher, W.A., Jolley, D., Carroll, B.I., Gomes, V.G., Jenkinson, A.V., McOrist G.D., 1999b. Selenium contamination, redistribution and remobilisation in sediments of Lake Macquarie, NSW. Organic Chemistry 30, 1287-1300.

Philibert, A., Gell, P.A., Newall, P., Chessman, B, Bate, N., 2006. Development of diatom-based tools for assessing stream water quality in south-eastern Australia: Assessment of environmental transfer functions. Hydrobiologia 572, 103-114.

Pienitz, R., Smol, J.P. and Birks, H.J.B., 1995. Assessment of freshwater diatoms as quantitative indicators of past climatic change in the in the Yukon and Northwest Territories, Canada. Journal of Paleolimnology 13, 21-49.

Poornima, E.H., Rajadurai, M., Rao, T.S., Anupkumar, B., Rajamohan, R., Narasimhan, S.V., Rao, V.N.R., Venugopalan, V.P., 2005. Impact of thermal discharge from a tropical coastal power plant on phytoplankton. Journal of Thermal Biology 30, 307-316.

Potapova, M.G., Charles, D.F., 2002. Benthic diatoms in USA rivers: distributions along spatial and environmental gradients. Journal of Biogeography 29, 167-187.

Potapova, M.G., Charles, D.F., 2007. Diatom metrics for monitoring eutrophication in rivers of the United States. Ecological Indicators 7, 48-70.

Powers, S., Tseitkin, F., Mehta, V., Lavery, B., Torok, S., Holbrook, N., 1999. Decadal climate variability in Australia during the twentieth century. International Journal of Climate 19, 169-184.

Powis,B.J., 1973. The effect of power station discharges upon benthic fauna. BSc (Hons) thesis School of Zoology, University of NSW.

Powis, B.J., Robinson, K.I.M, 1980. Benthic macrofaunal communities in Tuggerah Lakes, New South Wales. Aust, J. Mar. Fresh. Res. 31, 803-815.

Powles, P.M., 1974. Survival of Australian anchovy (*Engraulis australis*) eggs and larvae in a heat trap. In: The early life history of fish, Ed. J.H.S. Blaxter, Springer-Verlag, New York, p. 373-381.

Price, N.M., Thompson, P.A., Harrison, P.J., 1987. Selenium: an essential element for the growth of the coastal marine diatom *Thalassiosira pseudonana*. J. of Phycology 23, 1-9.

Rajadurai, M., Poornima, E.H., Narasimhan, S.V. Rao, V.N.R., Venugopalan, V.P., 2005. Phytoplankton growth under temperature stress: Laboratory studies using two diatoms from a tropical coastal power station site. Journal of Thermal Biology 30, 299-305.

Ralph, P.J., 1998. Photosynthetic response of laboratory-cultured *Halophila ovalis* (R. Br) to thermal stress. Marine Ecology Progress Series 171, 123-130.

Ralph, P.J., Wilson, K., Hill, R., Petrou, K., 2009. Effects of increased temperature pulses on temperate seagrass. Final Report. Institute for Water and Environmental Resource Management, University of Technology, Sydney, Australia.

Ralph, T.J., Kobayashi, T., Garcia, A., Hesse, P., Yonge, D., Bleakley, N. Ingleton, T., 2011. Paleoecological responses to avulsion and floodplain evolution in a semiarid Australian freshwater wetland. Australian Journal of Earth Sciences, 58: 75-91.

Rao, C.R., 1964. The use and interpretation of principal component analysis in applied research. Sankhya A 26, 329-358.

Reid, F.M.H, 1978. Chapter 5.5 Permanent Records. *In*: Sournia, A. (ed) Phytoplankton Manual, Monographs on Oceanic Methodology 6. UNESCO, Museum National d'Histoire Naturelle, Paris. Page Brothers, Norwich. ISBN 92-3-101572-9

Reid, M. A., 1997. A fine resolution palaeoecology of recent sediments from Lake Wellington, Gippsland lakes, Victoria. In: Proceedings 1st Australian Diatom Workshop 1-3 February 1997, 86-91. Deakin University School of Ecology and Environment.

Reid, M.A., Tibby, J.C., Penny, D., Gell, P.A., 1995. The use of diatoms to assess past and present water quality. Australian J. Ecology 20, 57-64.

Resende, P., Azeiteiro, U. and Pereira, M.J., 2005. Diatom ecological preferences in a shallow temperate estuary (Ria de Aveiro, Western Portugal). Hydrobiologia 544, 77-88.

Ridgway, K.R., 2007. Long-term trend and decadal variability of the southward penetration of the East Australian Current. Geophysical Research Letters 34, 1-5.

Ridgway K.R., Coleman, R.C., Bailey, R.J., Sutton, P., 2008. Decadal variability of East Australian Current transport inferred from repeated high-density XBT transects, a CTD survey and satellite altimetry. Journal of Geophysical Research Oceans 113, doi:10.1029/2007JC004664.

Ridgway, K., Hill, K., 2009. The East Australian Current. In: A Marine climate change impacts and adaptation report card for Australia 2009 (eds. E.S. Poloczanska, A.J. Hobday and A.J. Richardson, NCCARF Publication 05/09, ISBN 978-1-921609-03-9.

Ritchie, J.C., Ritchie, C.A., 1995. 137Cs use in erosion and sediment deposition studies: promises and problems. In: IAEA, Use of Nuclear Techniques in Studying Soil Erosion and Siltation. IAEA-TECDOC-828, 111-201.

Roach, A.C., 2005. Assessment of metals in sediments from Lake Macquarie, New South Wales, Australia, using normalisation models and sediment quality guidelines. Marine Environmental Research 59, 453-472.

Roach, A.C., Maher, W., Krikowa, F., 2008. Assessment of metals in fish from Lake Macquarie, New South Wales, Australia. Arch. Environ. Contam. Toxicol., 54: 292-308.

Robbins, J.A., 1978. Geochemical and geophysical applications of radioactive lead. In: Nriagu JO (ed) Biogeochemistry of lead in the environment. Elsevier Scientific, Amsterdam, pp. 285-393.

Roberts, B., 1994. The accumulation and distribution of selenium in sea mullet (*Mugil cephalus*) from Lake Macquarie, NSW, Australia. Honours thesis, University of Canberra, Canberra.

Roberts, D.E., Smith, A.R., Ajani, P., Davis, A.R., 1998. Rapid changes in encrusting marine assemblages exposed to anthropogenic point source pollution: a 'Beyond BACI' approach. Mar. Ecol. Prog. Series 163, 213-224.

Roberts, D.E., Barnes, P.B., 2004. Spatial and temporal variability in water quality and assemblages of phytoplankton in Tuggerah lakes, Lake Macquarie and Brisbane Waters. Report prepared for Wyong Shire Council by Bioanalysis – Marine, Estuarine and Freshwater Ecology, Narara, NSW, July 2004, pp.54.

Robinson, K, 1982. The structure of macrofaunal communities in Lake Macquarie, New South Wales. PhD thesis University of New South Wales.

Robinson, K.I.M., 1987. Effects of thermal power station effluent on the seagrass benthic communities of Lake Macquarie, a New South Wales coastal lagoon. Wetlands (Australia) 7, 1-22.

Round, F.E., Crawford, R.M. and Mann, D.G., 1990. The Diatoms: Biology and Morphology of the Genera. Cambridge University Press, Cambridge, U.K. ISBN 0 521 36318 7

Roy, P.S., 1981. Fossil Shell Assemblages in Lake Macquarie. Quarterly Notes: Geological Society of New South Wales 42, 12-17.

Roy, P.S., Peat, C., 1975. Bathymetry and bottom sediments of Lake Macquarie. Records, Geological Survey of New South Wales 17, 53-64.

Roy, P.S., Thom, B.G., Wright, L.D., 1980. Holocene Sequences on an Embayed High Energy Coast: An Evolutionary Model. Sedimentary Geology 26, 1-19.

Roy, P.S. and Crawford, 1984. Heavy metals in a contaminated Australian estuary – dispersion and accumulation trend. Estuarine, Coastal and Shelf Science 19, 341-358.

Roy, P.S., Williams, R.J., Jones, A.R., Yassini, I., Gibbs, J., Coates, B., West, R.J., Scanes, P.R., Hudson, J.P., Nichol, S., 2001. Estuarine, Coastal and Shelf Science 53, 351-384.

Sandström, O., 1990. Environmental monitoring at the Forsmarck nuclear power plant: Cooling water effects. Swedish Environmental Protection Agency, Environmental Impact Assessment Department, Uppsala 1991. pp.38. ISBN 91-620-3868-0

Saunders, K.M., McMinn, A., Roberts, D., Hodgson, D.A., Heijnis, H., 2007. Recent human-induced salinity changes in Ramsar-listed Orielton lagoon, southeast Australia. Aquat. Conserv. Mar. Freshw. Ecosyst. 17, 51-70.

Saunders, K.M., Hodgson, D.A., Harrison, J., McMinn, A., 2008. Palaeoecological tools for improving the management of coastal ecosystems: a case study from Lake King (Gippsland Lakes) Australia. Journal of Paleolimnology 40, 33-47.

Saunders, K.M., Taffs, K.H., 2009. Palaeoecology: a tool to improve the management of Australian estuaries. Journal of Environmental Management 90, 2730-2736.

Saunders, K., Lane, C., Cook, S., McMinn, A., Hallegraeff, G.M. 2010. Chapter 3: Benthic diatoms. *In*: Hallegraeff, Bolch, Hill, Jameson, Le-Roi, McMinn, Murray, de Salas and Saunders [eds] Algae of Australia: Phytoplankton of Temperate Coastal Waters. Commonwealth Scientific and Industrial Research Organisation (CSIRO) publishing, Melbourne, Australia, 432pp, Jul 2010.

Saunders, K.M., 2011. A diatom dataset and diatom-salinity inference model for southeast Australian estuaries and coastal lakes. Journal of Paleolimnology 46, 525-542.

Scanes, P., 1988. The impact of Eraring Power station on the fish and fisheries of Lake Macquarie. NSW Fisheries Institute. Report prepared for the Electricity Commission of New South Wales.

Simpson, S.L., Apte, S.C. and Batley, G.E., 1998. Effect of short-term resuspension events on trace metal speciation in polluted anoxic sediments. Environmental Science and Technology, 32, 620-625.

Simpson, S.L., Batley, G.E., Chariton, A.A., Stauber, J.L., King, C.K., Chapman, J.C., Hyne, R.V., Roach, A.C., Maher W.A., 2005. Handbook of Sediment Quality Assessment, CSIRO, Bangor NSW, 117 pp.

Smol, J.P., 1990. Paleolimnology: Recent advances and future challenges. Mem. Ist. Ital. Idrobiology 47, 253-276.

Snoeijs, P.J.M., 1991. Monitoring pollution effects by diatom community composition: A comparison of sampling methods. Archives Hydrobiologia 121, 497-510.

Snoeijs, P.J.M., Prentice, I.C., 1989. Effects of cooling water discharge on the structure and dynamics of epilithic algal communities in the northern Baltic. Hydrobiologia 184, 99-123.

Spencer, R.S., 1959. Some aspects of the ecology of Lake Macquarie, N.S.W., with regard to an alleged depletion of fish, II Hydrology. Australian Journal of Marine and Freshwater Research 10, 279-296.

Spliethoff, H.M., Hemond, H.F., 1996. History of toxic metal discharges to surface water of the Aberjona watershed. Environ. Sci. Tech. 30, 121-128.

Squires, L.E., Rushforth, S.R., Brotherson, J.D., 1979. Algal response to a thermal effluent: study of a power station on the Provo River, Utah, USA. Hydrobiologia 63, 17-32.

State of the Environment, 2006. Eds. Beeton, B.J.S., Buckley, K.I., Jones, G.J., Morgan, D., Reichelt, R.E. Trewin, D. Australia State of the Environment: Independent report to the Australian Government Minister for the Environment and Heritage, Commonwealth of Australia. ISBN 0642553009.

State Pollution and Control Commission (SPCC), 1983. Environmental Audit of Lake Macquarie, New South Wales State Pollution Control Commission (Department of Environment, Climate Change and Water) Report: December 1983, Sydney, pp. 159. ISBN 0 7249 5968 7.

Sullivan, M.J., 1999. In: Stoermer EF, Smol JPS (eds) The diatoms: applications for the environmental and earth sciences. Applied diatom studies in estuaries and shallow coastal environments, Cambridge University Press, Cambridge, pp 334–351.

Swaine, D.J., 1982. Trace inorganic constituents in fly ash. In: Symposium on coal combustion, University of Newcastle, New South Wales.

Taffs, K., Farago, L.J., Heijnis, H. and Jacobsen, G., 2008. A diatom-based Holocene record of human impact from a coastal environment: Tuckean swamp, eastern Australia. Journal of Paleolimnology, 39: 71-82.

Teixeira, T.P. Neves, L.M., Araujo, F.G., 2009. Effects of a nuclear power plant thermal discharge on habitat complexity and fish community structure in Ilha Grande Bay, Brazil. Marine Environmental Research 68, 188-195.

Telford, R.J., Birks, H.J.B., 2009. Evaluation of transfer function in spatially structures environments. Quaternary Science Reviews 28, 1309-1316.

Telford, R.J., and Birks, H.J.B., 2011. A novel method for testing the statistical significance of quantitative reconstructions inferred from biotic assemblages. Quaternary Science Reviews 30, 1272-1278.

Ter Braak, C.J.F., Šmilauer, P., 2002. CANOCO: Reference manual and CanoDraw for Windows user's guide: Software for Canonical Community Ordination (version 4.5). Microcomputer Power (Ithaca, NY, USA), 500 pp.

Ter Braak, C.J.F., 1986. Canonical correspondence analysis: a new eigenvector technique for multi-variate direct gradient analysis. Ecology, 67:1167-1179.

Thom, B., 1974. Coastal erosion in eastern Australia. Search 5, 198-209.

Thom, B.G., McLean, R.F., Langford-Smith, T., Eliot, I., 1973. Institute of Engineers Australia, National Conference Publication (73/1) 35.

Thom, B.G., Chappell, J., 1975. Holocene sea levels relative to Australia. Search 6, 90-93.

Thomas, I.M., Ainslie, R.C., Johnson, D.A., Offler, E.W., Zed, P.A., 1986. The effects of cooling water discharge on the intertidal fauna in the Port River estuary, South Australia. Transactions of the Royal Society of South Australia 110, 159-172.

Thompson, P., Baird, M.E., Ingleton, T., Doblin, M.A. 2009. Long-term changes in temperate Australian coastal waters: implications for phytoplankton. Marine Ecology Progress Series 394, 1-19.

Tibby, J., Reid, M.A., 2004. A model for inferring past conductivity in low salinity waters derived from Murray River (Australia) diatom plankton. Marine and Freshwater Research 55, 597-607.

Tibby, J., Gell, P.A., Fluin, J., Sluiter, I.R.K., 2007. Diatom-salinity relationships in wetlands: assessing the influence of salinity variability on the development of inference models. Hydrobiologia 591, 207-218.

Tibby, J., Tiller, D., 2007. Climate-water quality relationships in three Western Victorian (Australian) lakes 1984-2000. Hydrobiologia 591, 219-234.

Tibby, J., Taffs, K., 2011. Paleolimnology in eastern and southern Australian estuaries. Journal of Paleolimnology, 46, 503-510.

Touchette B.W., Berkholder, J.M., 2000. Overview of the physical ecology of carbon metabolism in seagrasses. Journal of Experimental Marine Biology and Ecology 250, 169-205.

Trabajo, R., Sullivan, M.J., 2010. Applied diatom studies in estuaries and shallow coastal environments. In: Smol, J.P., Stoermer, E.F., The Diatoms: Applications for the Environmental and Earth Sciences. Cambridge University Press, United Kingdom. pp.686.

Turak, E., Lloyd, K.F., Norris, R.H., Simpson, J., Waddell, N., 1999. Assessment of river condition at a large spatial scale using predictive models. Freshwater Biology 41, 283-298.

Underwood, A.J., 1989. The analysis of stress in natural populations. Biological Journal of the Linnean Society of 37, 51-78.

Underwood, A.J., 1997. Experiments in Ecology. Their logical design and interpretation using Analysis of Variance. Cambridge University Press, United Kingdom, 509 pp.

Underwood, G.J.C., 2005. Microalgal (microphytobenthic) biofilms in shallow coastal waters: How important are the species? Proceedings of the California Academy of Sciences 56, 162-169.

Underwood, G.J.C., Phillips, J., Saunders, K., 1998. Distribution of estuarine benthic diatom species along salinity and nutrient gradients. European Journal of Phycology 33, 173-183.

Van Dam, H., Mertens, A., Sinkeldam, J., 1994 A coded checklist and ecological indicator values of freshwater diatoms from the Netherlands. Netherlands Journal of Aquatic Ecology 28, 117-133.

Van den Wollenberg, A.L., 1977. Redundancy analysis. An alternative for canonical correlation analysis, Psychometrika 42, 207-219.

Vanormelingen, P., Verleyen, E., Vyverman, W., 2008. The diversity and distribution of diatoms: from cosmopolitanism to narrow endemism. Biodiversity Conservattion 17, 393-405.

Vinson, D.K., Rushforth, S.R., 1989. Diatom species composition along a thermal gradient in the Pontneuf River, Idaho, U.S.A. Hydrobiologia 185, 41-54.

Vos, P.C. and de Wolf, H., 1993. Diatoms as a tool for reconstructing sedimentary environments in coastal wetlands – methodological aspects. Hydrobiologia 269, 285-296.

Vyverman, W., Verleyen, E., Sabbe, K., Vanhoutte, K., Sterken, M., Hodgson, D.A., Mann, D.G., Juggins, S., Van de Vuver, B., Jones, V., Flower, R., Roberts, D., Chepurnov, V.A., Kilroy, C., Vanormelingen, P., De Wever, A., 2007. Historical processes constrain patterns in global diatom diversity. Ecology 88, 1924-1931.

Wallis, R.L., 1976. Aspects of the thermal tolerance of the tropical mussel *Trichomya hirsuta* L. – A multivariable approach. Australian Journal of Marine and Freshwater Research 27, 475-486.

WBM Oceanics, 2005. South east water quality project: Interpretation of water quality monitoring program results. Report for Bega Shire and Eurobodalla Shire Councils, 140pgs. R.N0938.004.01

Wear,, R.J., Tanner, J.E., 2007. Spatio-temporal variability in faunal assemblages surrounding the discharge of secondary treated sewage. Estuarine, Coastal and Shelf Science 73, 630-638.

Weckström, J. Korhola, A., Blom, T., 1997. The relationship between diatoms and water temperature in thirty subarctic Fennoscandian lakes. Arctic and Alpine Research 29, 75-92.

Weckström, K., Juggins, S, Korhola, A., 2004. Quantifying background nutrient concentrations in coastal waters: a case study from an urban embayment of the Baltic Sea. Ambio., 33: 324-327.

Weckström, K., Juggins, S., 2006. Coastal diatom-environment relationships from the Gulf of Finland, Baltic Sea, J. Phycology, 42: 21-35.

Wilmore, A., Sladden, T., Bates, L., Dalton, C.B., 2006. Use of geographic information systems to track smelter-related lead exposures in children: North Lake Macquarie, Australia, 1992-2002. International Journal of Health Geographics 5, 1-14.

Witkowski, A., Lange-Bertalot, H., Metzeltin D., 2000. Diatom flora of marine coasts. In: Lange-Bertalot H (ed) Iconographica Diatomologica: annotated diatom micrographs, Vol. 7. A.R.G. Ganter Verlag K.G., Berlin, 925 pp.

Winning, G., 1990. Lake Macquarie littoral habitats. Report of Shortland Wetlands Centre for Lake Macquarie Council.

Wong, D. and Olivera, L., 1991. Effects of selenite and selenate on the growth and motility of several species of marine microalgae. Canadian Journal of Fisheries and Aquatic Science, 48: 1193-1200.

Wood, E.J.F., 1959. Some aspects of the ecology of Lake Macquarie, NSW with regards to an alleged depletion of fish. VI. Plant communities and their significance. Australian Journal of Marine and Freshwater Research 10, 322-340.

Wood, E.J.F., Crosby, L.H., Cassie, V., 1959. Studies on Australian and New Zealand diatoms. III: Descriptions of further discoid species 87.

WBM Oceanics Pty Ltd, 1997. Lake Macquarie Estuary Management Study: Volume 2 – Lake Management Issues. Prepared for Lake Macquarie City Council rep: 9487.R5.4.

Zapata, F., 2002. Handbook for the Assessment of Soil Erosion and Sedimentation using Environmental Radionucleides. Kluwer Academic Publishers, The Netherlands. ISBN-1-4020-1041-9

Zhang, G.H., Hu, M.H., Huang, Y.P., Harrison, P.J., 1990. Selenium uptake and accumulation in marine phytoplankton and transfer of selenium to the clam *Puditapes philippnmarium*. Mar. Env. Res. 25, 179-190.

Zielinski, U., Gersonde, R., 2010. Diatom distribution in Southern Ocean surface sediments (Atlantic sector): Implications for paleoecological reconstructions. Palaeogeography, Palaeoclimatology, Palaeoecology 129, 213-250.

Web Appendices

Australian Bureau of Meteorology, 2010. http://www.bom.gov.au date accessed 11 November 2010.

Australian Bureau of Statistics, 2008. The production and trade of minerals. http://www.abs.gov.au/ausstats/abs@.nsf/0/12D42ED59A2793D8CA25773700169CC4?opendocument accessed 15 August 2011.

Australian River Assessment System (AusRivAS), eWater Cooperative Research Centre and Australian Government Department of Environment and Heritage and Land and Water Australia. http://ausrivas.canberra.edu.au accessed 10 February 2011.

Hammer, O., Harper, D.A.T., Ryan, P.D., 2001. PAST: Palaeontological statistics software package for education and data analysis. Palaeontologia Electronica 4(1): 9pp. http://folk.uio.no/ohammer/past/ 2009.

Juggins, S., 2010. C2 Craticula version 1.6.8. Software for ecological and palaeoecological data analysis and visualisation. University of Newcastle, Newcastle Upon Tyne, United Kingdom.

National Land and Water Resource Audit (NLWRA) 2002, Australian Catchment, River and Estuary Assessment 2002: Volume 1, National Land and Water Resources Audit, Canberra [nlwra.gov.au/files/products/national-land-and-water-resources-audit/pr020282/pr020282.pdf]

The National Library of Australia, 2011. Digitised newspapers – article dated Friday September 24, 1841. http://trove.nla.gov.au/ndp/del/article/12871295?searchTerm=ebenezer+AND+(threlkeld) accessed 21 June 2011.

NSW Department of Trade and Investment, 2011. Minerals and petroleum – NSW coal. http://www.dpi.nsw.gov.au/minerals/resources/coal accessed 10 October 2011.

NSW Minerals Council, 2011. Coal Specific Statistics. http://www.nswmin.com.au/Mining-in-NSW/Facts-and-Figures/Economic-Contribution/Coal-Specific-Statistics/default.aspx accessed 30 October 2011.

NSW OEH, 2008. Environment Protection Licence Number 761 and Annual Returns for Delta Electricity, Vales Point Power Station and Coal Unloader, Mannering Park, 29 pp. http://www.environment.nsw.gov.au/poeoapp/index.aspx

NSW OEH, 2008. Landuse: Eastern New South Wales - catchment land use major categories, Lake Macquarie, ESRI shapefile. Community Access to Natural Resource Information. New South Wales, Department of Premier and Cabinet, http://canri.nsw.gov.au/nrdd/records/ANZNSO359100121.html

NSW OEH, 2009. State of the Environment Report 2009. http://www.environment.nsw.gov.au/soe/index.htm accessed 20 June 2010.

NSW OEH, 2010. Coastal Eutrophication and Risk Assessment Tool (CERAT). http://www.environment.nsw.gov.au/research/cerat.htm accessed 12 January 2010.

OzCoasts, 2010